STUDIES ON THE COMPLEXES OF SOME TRANSITIONAL ELEMENTS

THESIS SUBMITTED IN FULFILMENT OF
THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY
IN CHEMISTRY

Department of Chemistry
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BY

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A C K N O W L E D G E M E N T

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A. U. Malik

C O N T E N T S

GENERAL INTRODUCTION

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Metals of transitional series, with their small cation size, comparatively large nuclear or ionic charge and characteristic property of building up p, d or f sublevels, show great affinity for combining with electron donors (restricted to strongly non-metallic elements of group V and VI) and thereby offer newer and more interesting aspect for original research work in the field of coordination chemistry. Many investigators, particularly Sidgwick[1], Pauling[2], Bailar[3], Calvin[4], Taube[5] etc., have drawn attention to many fundamental problems, viz., tendencies of various groups to form complexes, favourable conditions for chelation, relative tendencies of metals for combination with oxygen or nitrogen, the problem of the energy of d sub level visa-vis that of s or p orbitals, the role of paired or unpaired electrons in bond formation, problem concern with uncommon or abnormal valence states and coordination with hydroxyl group (specially that of phenolic) or nitrogen and hydroxyl together are of special interest and need more extensive work for elucidation of their nature, composition and structure. And this can be achieved by the coordination of purely physical and physico-chemical methods during their investigation.

The existing literature abound in references on the complexes of transitional elements, and the different aspects emerging from large experimental data accumulated, during the

last fifty years have been fully dealt with but the fact remains that much is to be done in the field of uncommon valence states. Here, ambiguity exists in theoretical considerations[6] and relatively small amount of work has been carried out on a number of lower and higher valence states. Considering members of the first transitional series it may be very well seen that although almost all the metals (except Cr (iii)) have been fully investigated, there is much scope for further investigations on the complexes and chelates of Mn(iii), V(iv), Cr(ii) and Cu(i).

What has been said about the uncommon valence states of some of the metals of the first transitional series is equally true for many complexing agents. Schwarzenbach[7] for the first time drew attention to the importance and practical utility of a series of compounds named as "Complexones" in analytical work. Investigations on these aminopoly carboxylic acids have given fresh impetus to research work in inorganic chemistry and a number of papers have been published in recent years. However, there are other sets of organic reagents susceptible to complex ion formation which have been less extensively investigated until now. Amongst them mention may be made of chromotropic acid and its substituted derivatives, ethanolamines and hydrazine.

Chromotropic acid (1,8 dihydroxy naphthalene, 3,6 disulphonic acid) is the most important of ten possible and known dihydroxy naphthalene sulphonic acids. It is prepared[8] by the action of alkali on 3,6,8 trisulphonic acid of α - naphthyl amine or α - naphthol, the latter synthesis gives a purer

product. Its use as valuble intermediate for the preparation of modern azo dyes and as a useful coupling component for the preparation of monoazodyes, is well established.[9] Of its early analytical uses mention may be made of the colour reaction[10] with formaldehyde in presence of sulphuric acid. Theoretical aspect concerning the study of this compound, however are of relatively recent origin and can be traced back as early as 1940.

The course of the last fifteen years have seen many intresting studies on the interaction of metals with chromotropic acid and its substituted derivatives. The most extensively investigated amongst these are those of Fe (iii) and Ti (iv). Hofmann[11] in 1912 mentioned about the possibility of the inter action of Ti (iv) with chromotropic acid. But the real understanding of the problem came from the work of L. Sommer and Coworkers[12] (who published about a dozen of papers on this very reaction), who studied the complex spectrophotometrically in the PH range 0 to 11 and showed the existence of 1:2, 1:3 complexes (TiR, TiR_2 TiR_3 , Ti(OH) R_3 etc.) in the extremely acidic to moderately basic range Sommer besides carrying out spectrophotometric investigations studied[13] polarographic behaviour of the complex in order to confirm his earlier results on the composition of the complex. The Fe (iii)- Chromotropic acid complex was also investigated extensively by a number of eminent workers including Heller and Schwarzenbach[14], Bensck[15] etc. According to Schwarzenbach, a six membered ring is formed during the complex formation with 1:1 ratio of the reactants. The value

of log K for the first OH and the second OH were found 5.36 and 15.6 respectively and the formation constant was found to be 17 ± 0.5. Bensck confirmed the results on the basis of his polarographic study on this complex.

E.D.T.A. is supposed to be a very useful reagent in complexometry. But there appears to be some doubt regarding its superiority to chromotrophic acid. Schwarzenbach[16] in his "Die Komplexometrische Titration" has given an intresting account on the utility of this reagent (chromotrophic acid) and its superiority over complexones like E.D.T.A. According to him " the Cations of the elements like B, Be, Ti, Ge, Nb and Ta show slight tendency to coordinate through nitrogen of a complexone, moreover, the carboxylate groups of complexones are manifestly too bulky for small cations. Considering these limitations, polyphenols would be intrinsically more favourable in such cases. But these too cannot be satisfactorily employed as complexing partners, since the rigid structure of the aromatic ring system prevents more than two phenolic hydroxyl groups to coordinate with the metal cation. Under the circumstances, the best chelating agent for B, Be, Ti, Ta and Ge would be pyrocatechol (e.g. , Tiron) or 1, 8 dihydroxy naphthalene 3, 6 disulphonic acid (e.g., chromotrophic acid)."

Amongst the substituted 1,8 dihydroxy naphthalene disulphonic acids, p nitrobenzene azo chromotropic acid (4,5 dihydroxy 3 p-nitro phenyl azo- 2,7 naphthalene disulphonic acid) commercially known as Chromotrope 2B has long been used[17] as a colorimetric reagent for boric acid. Like chromotropic acid, it is also used[18] as a dyeing constituent for cotton and wool. So far as its utility as a complexing agent is concerned, it is

least understood and very few metals have been tried to undergo complex formation with this reagent. Complex ion formation with this reagent is however, possible inspite of the fact that the donor property of the azo group are weak. But since, the compound contains a strong donor (e.g. hydroxyl group) in a position ortho to azo group, very stable chelate rings are likely to exist and the complexes so formed should be highly stable, coloured and find use as dye and pigment.[19] The reagent has an extra advantage in having an esterifiable phenolic hydroxyl group in coordination position with respect to nitrogen of the azo group, but evidence for chelation through this group is not forthcoming.

Sommer and Hnilickova[20] had reviewed the analytical applications of azo chromotropedyes. Chromotrope 2B is found to give colour reaction with Cr (ii)[21] and Tl (iii)[22]. More recently Banerji and Dey[23] studied Thorium complex spectrophotometrically and showed the formation of 1:2 metal-chromotrope 2B chelate. They also calculated the values of formation constant, log K=10.08 $\pm$ 0.5 and free energy $-\Delta F^{o}$= 13.92- Kcals at 25°.

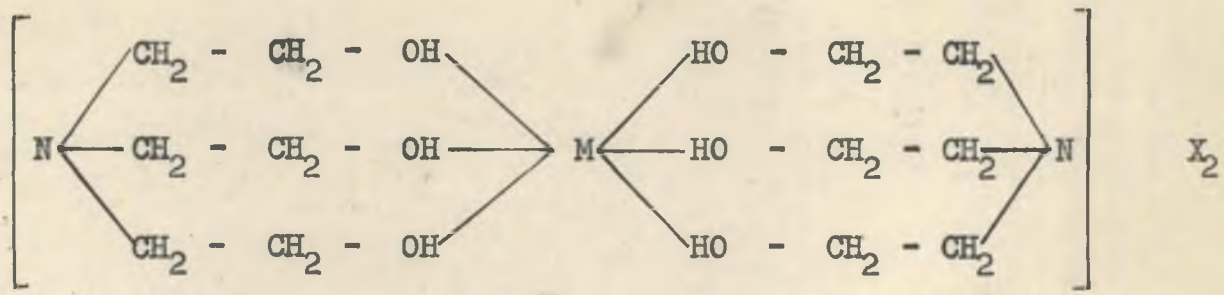
8 hydroxy quinoline, 7 iodo, 5 sulphonic acid, better known as Ferron, is a colorimetric reagent for iron belonging to substituted 8, hydroxy quinoline type of compounds. Yoe[24] first suggested its use for the determination of iron. Since then a number of papers have appeared in the literature on the composition and stability of Fe (iii) complex. This compound was extracted by combining it with tributyl amine and finally

extracting it with amyl alcohol in the pH range 2 to 7.[25]

The strong complex forming capacity of this reagent has been attributed to the presence of substituted quinoline ring since nitrogen of quinoline possesses very weak donor property.[26] The presence of Nitrogen, hydroxyl, sulphonic and iodide groups may all responsible for its complex forming tendency. Inner complex formation, however, is only possible through the nitrogen of quinoline and hydroxyl group. Comparatively little amount of work has been done on the metal complexes of Ferron. Few references are available on the use of this reagent in the detection of metals like Bi,[27] Tl[28] and Co[29]. It has also been successfully employed[30] in the separation of plutonium from uranium and other fission products.

Ethanol amines (amino derivatives of ethyl alcohol) can coordinate either through oxygen or nitrogen depending upon the metal ion. Almost all the metals have been tried but extensive studies particularly related with their structural complexities are lacking.[31] The addition of ethanolamines to concentrated aqueous solutions of metallic salts results in two types of compounds: (i) pure addition compounds (one mole of salts to two of the base) found as coloured crystals e.g., those with Ni, Cu, Sr and Mg chlorides; Ni, Cd, Cu sulphates; $NiBr_2$, $Cu\ I_2$ and $Ni\ (No_3)_2$ and $Pb\ Ac_4$ (ii) compounds where one or more of hydrogen atom of the hydroxyl group are substituted by the metal ion[32]. Tettamanzi and Carli[33] found that coordination compounds

rather than basic salts are formed with Ni, Cd, Mg and Ca. They proposed the alternative structure I and II.



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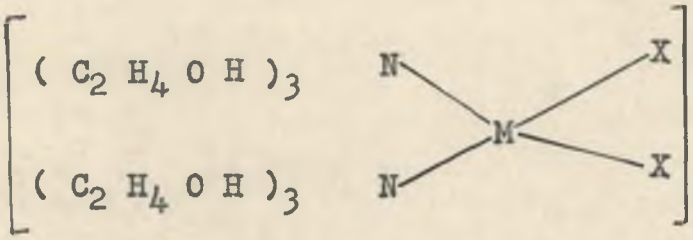

II

Various physical methods have been employed to study the behaviour and composition of ethanolamine complexes. Subrahmanya[34] observed that ethanolamines are reduced reversibly in ammonical solutions while in non ammonical solutions, reversible waves could be realised only in the case of triethanolamine. Michelle Gilband[35] studied the effect of pH on the complexing action of the triethanolamine on the copper salts. Molecular or ionised form of the complexes were

obtained depending upon the pH of the medium. Spectrophotometric and cryoscopic methods were also employed to study the copper complexes.

Ethanolamines, particularly triethanolamine, has been widely used in analytical chemistry as a masking agent for a number of metals. Pribil[36] had suggested its use as a masking agent for Al, Fe, Ti and Mn, while titrating Ni with E.D.T.A. in ammonical solutions and also that for Fe(iii) and Mn(ii) in the titration of calcium. Triethanolamine acts as a useful indicator in ascertaining the end point (sharp change from red to blue) while titrating lead against E.D.T.A.

The utility of ethanolamine in industry is also not less impressive. The toxicity of cyanide baths in electrodeposition units can be considerably reduced by using these compounds as bath materials.[38,39,40] Electrodeposition of copper and nickel on Zinc plates is very successfully carried out in their presence.[41]

Complex ion formation with hydrazine has been less extensively studied than in the case of other compounds having nitrogen as the donor. For some time this compound was considered to be useful only in synthesising organic compounds like hydrazide, aliphatic diazo compounds and organic ammonia derivatives. Today its utility and importance is much more recognised than even before by virtue of its strong reducing property, its use in the preparation of fuels and rockets[42] and finally its tendency to form stable coordination and addition compounds especially with metals in the lower oxidation or valence state.

A large number of metal-hydrazine complexes including those of Ag,[44] Hg,[45] Pt,[46] Ru,[47] Cr,[48] Ni,[49] Cu[50] etc. have been studied and the following conclusions regarding their nature and composition have been drawn.[51]

(i) Hydrazine forms many coordination compounds though their number are somewhat limited because of its reducing action.

(ii) Except the complexes with Pt, Ru the compounds of hydrazine with other metals in their higher oxidation states are limited in number and unstable e.g. Cr(iii), Co(iii), Ce(iv), etc.

(iii) Most of the hydrazine complexes which have been isolated as solid do not contain enough hydrazine to fill the coordination sphere so it has been suggested that hydrazine acts as a bidentate group.

(iv) Since no structural determination has been made, the existence of three membered chelate ring is not confirmed. Moreover, no well authentic case of optical isomerism which might be used as evidence for a chelate ring structure has been observed with hydrazine complexes.

(v) In many cases hydrazine has been reported to act as a monodentate group as in case of platinum complexes. According to Bailar,[52] Zinc coordinates four hydrazine molecules with only small differences between the seperate dissociation constants. This indicates that hydrazine is monodentate, with four coordinate zinc ions.

(vi) Low solubility indicates poly nuclear rather than chelate structure e.g., Ru and CrI_2 complexes.

(vii) Unstable valence states of metals are stabilised by hydrazine in certain cases e.g., Cr(ii).

The conventional method of chemical analysis sometimes fails to give the correct picture of the composition of complex compounds. This is specially so when dealing with compounds of insoluble character since their isolation is difficult in the pure form. Almost all hydrazine complexes are insoluble and hence the results obtained by the method of chemical analysis need furthur confirmation by other methods. The results on hydrazine complexes have also to be considered from this point and the earlier work needs confirmation and support by physical methods. In this connection mention may be made of Schwarzenbach and Zobrist[53] who employing Bjerrum technique have shown that four moles of hydrazine and nickel with six. Bailar (loc-cit) had also shown the existence of tetrahydrazinate in the case of Zinc polarographically.

In the preceding paragraph attention was drawn to the stabilising tendency of hydrazine towards lower valence ions. Another striking illustration of this behaviour is provided by the halo complexes of Cu (i), where stabilisation is achieved by coordination through halide ions. A survey of the early work in this field reveal that most of the studies were limited only to the determination of solubility of cuprous halide in alkali halide solutions.[54] [55] With the introduction of physical methods, more reliable data were available for

study the nature of the complexes formed. The work of Remy and Labes[56], Szabo and Szabo[57] on the chloro complexes of Cu(i) bear testimony to this statement. The latter authors determined analytically and potentiometrically the composition of the solution obtained by dissolving copper anodically in solutions of KCl, NaCl, HCl, K Br etc. In chloride solutions they found that Cu Cl_3 is formed above 0.04M Cu concentration. Recently Malik and coworkers[58] carried out investigation to deermine the complex formation in systems like Cu Cl-HCl-H_2O, Cu Cl-KCl-H_2O both in the aqueous and solid phases empolying analytical and electrometric methods. They developed a new method based upon the indirect determination of solid phase by drawing solubility curves on rectilinear coordinates.

Although, enough work has been done on the chlorocomplexes of Cu(i), very little is to be found in the literature on the bromo and iodocomplexes. C.M. Harris[59] made an extensive study of bromo-iodocuprates by dissolving Cu I in concentrated ammonium or alkali bromide and isolated the compounds $Cu(NH_3)_4$ Cu I Br_2 (black), $Cu(en)_2$ Cu I Br_2 (purple) and $(Cu\ I)_2\ NH_3$ (white palates). Wells and Hurlbert[60] prepared ammonium cuprotribromide $(NH_4)_2\ CuBr_3$, by mixing hot solutions of an excess of NH_4 Br with CuBr and HBr in presence of copper wire. Fleurent[61] prepared triammino Cuprotric bromide NH_4 Br 2 CuBr 2 NH_3 and polassium bromo Cuprate $KCuBr_3$ and described its properties. Recently, the bromo complexes of Cu (i) were

studied by Rehman and Malik[62] by considering the systems CuBr- HBr-H_2O, CuBr- KBr-H_2O and CuBr- $MgBr_2$ - H_2O.

In the preceding pages, various aspects concerned with the physico-chemical studies on aromatic hydroxy sulphonic acids, their substituted derivatives, ethanol amines and hydrazine, have been briefly disussed, there it was said that these compounds besides being industrially useful, had found great utility in analytical chemistry. Attention was drawn to the fact that these compounds represented a rare group of coordinating agents whose metal complexes have yet to be studied systematically. Approach to this problem can be made in two directions (i) study of the complexes of such metals which have not either been studied or on which very little has been done till now; (ii) application of various physico-chemical methods (ranging from-the older technique of chemical analysis, conductometry and potentiometry to the more recent ones like spectrophotometry, polarography, amperometry, coulometry etc.) to those compounds which need further investigation for understanding their real nature.

The work described in the thesis deals with the following aspects of the problem:

(1) Composition of the soluble complexes of Cu(i), Cu(ii), Mn(iii) and V(iv) with chromotropic acid; of Cu(ii) with chromotropic 2B-and of V(iv) with Ferron, employing spectrophotometric, polarographic, conductometric and potentiometric methods

(2) Study of the interaction of vanadyl ion with monodi and tri-ethanolamines by spectrophotometry and amperometry.

(3) Physico-chemical studies on Cr(ii and iii) hydrazine complexes.

In all the above three cases methods of chemical analysis and, wherever possible, magnetic measurement results were employed for the characterisation of the different compounds.

The last chapter of the thesis deals with a lesser known aspect of the problem on the halo complexes of Cu(i). These studies were carried out by studying the system CuBr-KBr-H_2O, CuBr-HBr-H_2O and CuBr-$MgBr_2$-H_2O. The results on phase rule studies have been supplemented by the result on conductometry and potentiometry.

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C H A P T E R I.

Complexes of Chromotropic Acid (sodium salt) with Cu(i), Cu(ii), Mn(iii) and V(iv).

COMPLEXES OF CHROMOTROPIC ACID (SODIUM SALT) WITH Cu(i), Cu(ii), Mn(iii) AND V (iv)

The problem of interaction of metal ions with dyes (formation of dye lakes) has attracted much attention in recent years. These lakes are of two types: (i) forming Coordination Compounds (ii) giving ordinary salts of dyes. 1,8 dihydroxy naphthalene 3,6 disulphonic acid (chromotropic acid) is said to form both types of compounds. The existence of metal complexes has been indicated not only in metals of the first transitional series but colour reactions with metals like Hg (i and ii), Au (iii)[2], Ag[3], Pb[4], Sn[5], etc. have also been reported. Detailed data are available only in the case of Fe (iii) and Ti (iv) complexes. Besides, the pioneering work of L. Sommer and Schwarzenbach[8] (already cited vide general introduction) on the complexes, mention may be made of the work of W. Brandt[6], I.K. Babko and O.I. Popva[7]. Brandt et al noticed a variety of coloured products formed during the reaction of Ti (iv) with chromotropic acid depending upon the acidity of the solution. Babko and Popva suggested the use of this reagent for Ti (iv) determination.

Amongst other metal complexes, worth mentioning are those of UO^{++}[9], Cr^{+++} and Be^{++}. The reaction of Uranyl ions with

chromotropic acid has been utilized not only for its colorimetric estimation but also to know the nature of the complex (1:1 complex)[10]. Garret[11] has reported the reaction of Cr (iii) with chromotropic acid. Lukin and Zavarikina[12] has suggested its use a colorimetric reagent for beryllium.

From what has been said above it is apparent that there are number of metal ions which have not yet been fully studied and deserve a detailed investigation. One such example is that of Cu (ii). This metal ion forms a red coloured complex with chromotropic acid (sodium salt), the reaction being a slow one taking 6 to 12 hours for completion. But apart from the preliminary investigations of Martell and Coworkers[13], nothing substantial has been done so far and a detailed study of the compound is worth undertaking.

The problem of investigating chromotropic acid complexes with metal ions in their uncommon valency states is also worth considering. For this purpose Cu (i), Mn(iii) and V (iv) may be chosen like Cu (ii), both Cu (i) and V(iv) react slowly with chromotropic acid, vanadium giving a red coloured product while with Cu (i) a pink compound is obtained. Of these two complexes only one of them V(iv) has been studied[14] to some extent, but details are lacking. In the case of Mn (iii)

the reaction is almost instantaneous and proceeds smoothly in highly acidic medium.

The work described in the present chapter covers the following physico-chemical aspects of the problems. (i) Spectrophotometric studies on the composition of Cu(i), Cu(ii), Mn(iii) and V(iv) complexes. The composition of the complex was determine (i) Job's method of continuous variation[15] (ii) slope ratio method[1] and (iii) modified slope ratio method.[17,18] Before, actually carrying out the absorption experiments Vosburgh and Cooper's method[19] was applied in order to know the number of complexes existing in the solution.

(ii) Conductometric studies on the composition of Cu(i) complex. The conductometric measurements were made with mixtures prepared according to Job's method of continuous variation.[20,21]

(iii) Potentiometric studies on Mn(iii) - chromotropic acid compl employing Mn(ii) $\rightleftharpoons$ Mn(iii) + e couple as the indicator electrode.

(iv) Polarographic investigations on Cu(ii) - chromotropic acid complex.

E X P E R I M E N T A L

S O L U T I O N S

Cuprous Chloride Solution:

Cuprous chloride was obtained by reducing cupric chloride by copper turnings in presence of concentrated HCl.

About 10 grams of cupric chloride (reagent grade) was dissolved in about 75 cc of conc. HCl contained in a flask. 15 gms of metallic copper (in the form of fine turnings) were then added and the solution was warmed, until the dark colour was disappeared. The resulting colour-less solution thus obtained was poured in a litre of cold water contained in a beaker of 2 litres capacity. The pouring was done through a funnel whose neck was loosely plucked with a little glass wool to retain small particles of undissolved copper or other impurities. The cuprous chloride was atonce separated out and after stirring well, was allowed to settle and then washed twice with water containing a little amount of HCl. The precipitated product was filtered off by means of sunction pump. First it was washed with dil sulphurous acid (obtained by passing SO_2 into water) in order to check the rapid oxidation of the product. Then it was washed with glacial acetic acid so that water molecules adhering to cuprous chloride were removed. It was then washed several times with absolute alcohol (using 25 cc of aliquot each times) and finally washing with ether to remove the last traces of alcohol.

The cuprous chloride after finally washing with ether was kept in vacuum desiccator over CaO which was subjected for the complete evaporation of ether.

An approximate solution of strength (0.01M) was prepared by dissolving about 0.1 g of the substance in 0.1M KCl (AnalaR). This solution was left under a layer of paraffin to avoid oxidation. The strength of the solution was determined by estimating it gravimetrically as cuprous thiocyanate.

A known valume of the cuprous chloride solution was taken in a beaker and was slightly warmed, and a freshly prepared (1% NH_4CNS) was added slowly with constant stirring, from a burette until present in a slight excess. The precipitate of cuprous thiocyanate was white in colour. The precipitate was allowed to settle for several hours and then filtered through a weighed sintered orucible. The precipitate was washed ten to fifteen times with ice cold double distilled water (containing 1 cc of 1% NH_4CNS solution) and finally washed with 20% alcohol to remove ammonium thiocyanate and the precipitate was dried to constant weight at 110° - 120° and weighed as $Cu_2(CNS)_2$.

Manganic Sulphate Solution:

Manganic sulphate solution was obtained by the oxidation of Manganous sulphate with $KMnO_4$ in presence of sulphuric acid.

The method recommended by Ubbelehode[22] with slight modifications was followed:

15.1 gms of manganous sulphate was dissolved in 1 litre of 6N sulphuric acid. To 50 cc of this solution an other 3 cc of concentrated acid were added and the mixture kept in the ice bath. 12 cc of 0.5 N potassium permanganate were then added in aliquots of 2 cc, at an interval of about three minutes. A further 2 cc of conc. H_2SO_4 were added in between. Attempt to prepare solutions of higher concentration than 0.07M met with failure. To avoid formation of higher oxides in the solution it was found safer to add double the amount of sulphuric acid, as recommended by Ubblehode (loc. cit.).

The strength of manganic sulphate solution was determined by titrating against ferrous ammonium sulphate solution of known strength. The end point was detected by the change in colour from light green to yellowish green. A jump in potential of about 0.35 volt was observed at the end point on the addition of a single drop of the titrant. The strength of the solution was found to be 0.018M.

Vanadyl Sulphate Solution:

Vanadyl sulphate (Riedel) was used for the experiments A 0.01M solution of the reagent was prepared by dissolving 0.8150 of the substance in 500 cc of double distilled water and the

strength of the solution was determined[23] volumetrically by reducing it on Jone's reductor and titrating it against potassium permanganate solution. The following procedure was adopted:

The vanadyl sulphate solution containing sulphuric acid was treated with 0.1N $KMnO_4$, to produce a pink colour and was then passed through a Jone's reductor, where upon it was reduced to the bivalent state, the reduced solution was passed in an excess of an acidified solution of Ferric ammonium sulphate AnalaR) and the ferrous iron thus formed was titrated with standard 0.1N $KMnO_4$.

Cupric Chloride Solution:

Cupric chloride (AnalaR) B.D.H. was employed during the experiments. A 0.01M solution of the salt was prepared by dissolving 0.8527 g of cupric chloride in 500 cc of air free double distilled water.

The strength of the cupric solution was determined by titrating it iodometrically against thio-sulphate solution, using starch as indicator.

Chromotropic Acid Solution:

Chromotropic acid (sodium salt) of E. Merck (reagent grade) was used for the experiments 1.00759 gm of the substance was dissolved in 250 cc of air free distilled water and thus a solution of concentration 0.01M was obtained. As the reagent was highly sensitive to light, it was kept in amber coloured bottles, coated with thin black paper sheets. Fresh solutions of the reagent were prepared for each set of the experiment.

Preparation of the Buffer Solutions:

Standard Buffers solutions were prepared[24] for spectrophotometric and polarographic studies. The following standard Buffer solutions were used during the experiments.

1. McIlvaine Buffer (Na_2HPO_4 and citric acid) for the pH range 2.2 - 8.0.

2. Walpola Acetate Buffer (Sodium acetate and acetic acid) for the pH range 3.7 to 5.6.

3. Sørensen Buffer (NaH_2PO_4 and Na_2HPO_4) for the pH range 5.91 - 8.0.

4. Sørensen Buffer (Glycine (in NaCl) and NaOH) for the pH range 8.2 - 10.0.

5. Ringer Buffer (NaOH - NaH_2PO_4) for the pH range 11.5-12.0

All the Buffers were prepared from A.R. products.

The pH of the buffers were checked with the help of Beckman pH meter (model G) with Beckman glass electrode of general utility upto pH 10 and Beckman E type glass electrode after pH 10.

Spectrophotometric Studies on Cu(i), Cu(ii), Mn(iii) and V(iv) Complexes.

The spectrophotometric method is especially suited to the study of the complexes not sufficiently stable to permit their isolation from solution. In recent years a simple colorimetric method has been used to determine the composition of such complexes. This technique was called the method of continuous variation, introduced by Job (loc. cit.). Considering the formation of a complex A Bn where A is a metallic ion and B is a coordinating agent:

$$A + n\,B \rightleftharpoons A\,B_n$$

$$K = (A\,B_n) / (A)\,(B)^n$$

where ( ) represents activities $\approx$ molar concentrations. If we impose the restriction

$$(A) + (B) = C$$

where C is a constant, it can be shown that when concentration

$A B_n$ is a maximum

$$(B) / (A) = n$$

or $$d(A B_n) / d(A) = 0$$

In other words, for a constant total concentration of metal and coordinating agent, the concentration of complex is greatest when the metal and complexing agent are brought together in the same ratio in which they exist in the complex. If the complex is the only coloured substance present, the optical density of the solution is proportional to complex concentration. Hence a plot of optical density versus composition of the solution under the restriction imposed would give a curve with a maximum at the composition corresponding to the formula of the complex. If substances are present which absorb light in the same region as does the complex, it is necessary to make allowance for this. In such a case the difference in optical densities between the complex and the estimated amounts of uncomplexed coloured substances present may be plotted as a function of the concentration. Ordinarily the optical density that would have resulted if no complex formation had taken place is subtracted from the observed optical density and the difference is plotted against composition. Job[25] stated that the method was not generally applicable to systems in which more than one compound was formed. Vosburgh and Coworkers were later able to apply it to a special case in which they determined the nature of equilibria involving three chelate compounds. These

authors have studied[25] the complexes of Ni^{++} with O-phenanthroline and ethyl diamine formed in 1:1, 1:2 and 1:3 proportions and copper ammonia complexes (ratio Cu^{++} : NH_3 as 1:2 and 1:4) and thus confirmed the validity of the new method.

An other method, which is generally used in spectrophotometric measurements is the slope ratio method. This method is useful in two ways: it provides a confirmation of the results of Job's method of continuous variation and it also helps in establishing the composition of the complex e.g., the ratio of coordinating agent to the metal ions. In the reactions $mA + nB \rightleftharpoons A_m B_n$ if the concentration of B is kept constant and is in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex ($A_n B_n$) will be essentially proportional to the total concentration of A added; s

$$A_m B_n = C_A / m \qquad (1)$$

From Beer's Law $E = ed\,(A_m B_n)$ (2)

where E is the measured extinction, e the molecular extinction coefficient and d the thickness of the cell in cm. Substituting the value of ($A_m B_n$) from (1) and (2)

$$E = ed.\ C_A/m \qquad (3)$$

If E is plotted against different analytical (or total) concentrations of A, keeping the concentration of B constant and in excess. The equation (3) is valid over the straight line

portion of the curve and this straight line will give a slope represented by

$$\text{Slope}_1 = ed/_m \qquad (4)$$

similarly if A is the component in constant excess and the concentration of B is varied

$$A_m B_n = C_{B/n} \qquad (5)$$

and if E is plotted against C_B, the slope of the straight line protion of the curve will be

$$\text{Slope}_2 = ed/_n$$

The ratio of n to m in the complex may be determined by taking the ratio of two slopes

$$\frac{\text{Slope}_1}{\text{Slope}_2} = \frac{n}{m}$$

In the modified slope ratio method[17,18] the absorbancies of the solutions are plotted against the concentration of the variable components from either end of the x-axis. The point of intersection of the two curves corresponds to the composition of the complex, assuming that only one complex is formed.

Spectrophotometric studies on Cu(i)-Chromotropic acid complex:

The reaction between cuprous chloride and chromotropic acid was a slow one and took about 6 to 12 hours before completio depending upon the concentration of the reactants used. Thus

with dilute solutions (Conc. 2.5×10^{-3} M to 1×10^{-3} M) it took about twelve hours to reach completion where as with relatively concentrated solution (1×10^{-2} M to 2.5×10^{-3} M) the upper limit was six hours.

Cuprous chloride and chromotropic acid (sodium salt), both of equal concentration (2×10^{-3} M) were mixed in the following ratios:

ratio	2:8	3:7	4:6	5:5	6:4	7:3
Cu^{+}	2 cc	3 cc	4 cc	5 cc	6 cc	7 cc
Chromotropic acid(Nasalt)	8 cc	7 cc	6 cc	5 cc	4 cc	3 cc

After keeping the solutions for more than six hours, the absorbances were measured.

All the absorption measurements were carried out with Bausch and Lomb 'Spectronic 20' after allowing sufficient warming up period for the instrument. Measurements above 650 mμ were made by introducing red filter.

Table I

Set I. Concentration of CuCl = 2×10^{-3} M

Concentration of D.N.S. = 2×10^{-3} M more than

O.D. was meanured after keeping the mixtures for six hours.

Wave length	Ratio of cuprous chloride to D.N.S.					
mμ	2:8 (Curve a)	3:7 (Curve b)	4:6 (Curve c)	5:5 (Curve d)	6:4 (Curve e)	7:3 (Cur
400	0.46	0.70	0.44	0.50	0.64	
410	0.48	0.58	0.36	0.31	0.52	1.5
420	0.48	0.54	0.28	0.27	0.42	1.2
430	0.58	0.60	0.68	0.85	1.5	2.0
450	0.45	0.50	0.29	0.26	0.37	0.9
475	0.30	0.50	0.30	0.22	0.36	0.8
500	0.32	0.46	0.29	0.27	0.24	0.6
525	0.28	0.45	0.28	0.23	0.22	0.6
550	0.22	0.28	0.23	0.18	0.19	0.4
575	0.07	0.21	0.13	0.10	0.10	0.2
600	-	0.16	0.08	-	-	0.2

Fig. 1.

Optical density measurements carried out in the range 400 m to 600 mμ, showing only one maxima at 430 mμ for the Cu (i)- DNS mixtures mixed in the proportion of cuprous chloride to DNS as 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 respectively.

For determining the composition of complex formed between cupro and D.N.S., Job's method of continuous variation was employed. The following sets of mixture were prepared.

Set No. I.

0.5 cc, 1.0 cc, 1.5 cc, 2.0 cc, 2.5 cc, 3.0 cc, 3.5 , 4.0 cc and 4.5 cc of CuCl mixed with 4.5 cc, 4.0 cc, 3.5 cc, 3.0, 2.5 cc, 2.0 cc, 1.5 cc, 1.0 cc and 0.5 cc of DNS respectively. The concentration of both the reactants was 2.5×10^{-3} M. After keeping the mixtures for about six hours, the optical densities of the solutions were measured.

Set II. Concentration of the reactants being 2×10^{-3} M and the reaction mixtures were kept for over six hours before performing optical density measurements. All other details being the same as in Set. I.

Set III. Concentration of the reactants = 1.25×10^{-3} M and the optical density measurements were performed after keeping for about 9 hours.

and Set IV. Concentration of the reactants = 10×10^{-3} M and the O.D were noted after keeping the solutions for about 12 hours.

The absorbances of the reactants e.g. CuCl and D.N.S. were found to be negligible at this wave-length viz., 430 m .

Curves were plotted between the O.D of the mixtures and the ratio $\frac{Cu^{+1}}{Cu^{+1} + D.N.S.}$ at 430 mμ.

Table 2.

Wave length 430 mμ.

Set I.			Set II.		
Vol. of CuCl	Vol. of DNS	O.D. of the mixture	Vol. of CuCl	Vol. of DNS	O.D. of the mixture
0.5 cc	4.5 cc	0.58	0.5 cc	4.5 cc	0.30
1.0 cc	4.0 cc	0.58	1.0 cc	4.0 cc	0.32
1.5 cc	3.5 cc	0.60	1.5 cc	3.5 cc	0.40
2.0 cc	3.0 cc	0.68	2.0 cc	3.0 cc	0.54
2.5 cc	2.5 cc	0.85	2.5 cc	2.5 cc	0.80
3.0 cc	2.0 cc	1.50	3.0 cc	2.0 cc	1.10
3.5 cc	1.5 cc	2.0	3.5 cc	1.5 cc	1.40
4.0 cc	1.0 cc	1.0	4.0 cc	1.0 cc	1.20
4.5 cc	0.5 cc	0.90	4.5 cc	0.5 cc	0.80
(Fig. 2, Curve 1)			(Fig. 2, Curve 2).		

Table 3

Wave length 430 mμ.

Set II.			Set III.		
Vol. of CuCl	Vol. of D.N.S.	O.D. of the mixture	Vol. of CuCl	Vol. of D.N.S.	O.D. of the mixture
0.5 cc	4.5 cc	0.08	0.5 cc	4.5 cc	0.10
1.0 cc	4.0 cc	0.12	1.0 cc	4.0 cc	0.10
1.5 cc	3.5 cc	0.16	1.5 cc	3.5 cc	0.10
2.0 cc	3.0 cc	0.28	2.0 cc	3.0 cc	0.12
2.5 cc	2.5 cc	0.60	2.5 cc	2.5 cc	0.18
3.0 cc	2.0 cc	1.0	3.0 cc	2.0 cc	0.48
3.5 cc	1.5 cc	1.20	3.5 cc	1.5 cc	0.85
4.0 cc	1.0 cc	0.94	4.0 cc	1.0 cc	0.46
4.5 cc	0.5 cc	0.70	4.5 cc	0.5 cc	0.50
(Fig. 2, Curve 3)			(Fig. 2, Curve 4)		

The composition of CuCl - D.N.S. complex determined by the Job's method of continuous variation, was further investigated by the slope ratio method.

The results are as follows:

Table 4.

Set I. Vol. of 5×10^{-3} M D.N.S. = 2.5 cc

Strength of CuCl = 2.5×10^{-3} M

Mixtures were kept for six hours to ensure complete reaction and then diluted to 5 cc.

Set II. Vol. of 5×10^{-3} M CuCl = 2.5 cc

Strength of D.N.S. = 2.5×10^{-3} M

Mixtures were kept for six hours to ensure complete reaction and then diluted to 5 cc.

Wave length 430 mμ:

Set I.		Set II.	
Vol. of CuCl	O.D.	Vol. of D.N.S.	O.D.
0.0 cc	0.50	0.0 cc	0.96
0.1 cc	0.50	0.1 cc	1.0
0.2 cc	0.52	0.2 cc	1.1
0.3 cc	0.56	0.3 cc	1.1
0.4 cc	0.58	0.4 cc	1.2
0.6 cc	0.60	0.6 cc	1.3
0.8 cc	0.70	0.8 cc	1.4
1.0 cc	0.74	1.0 cc	1.5
1.2 cc	0.84	1.2 cc	1.6
1.4 cc	0.92	1.4 cc	1.8
1.6 cc	0.90	1.6 cc	2.0
	Fig. 3, Curve 1.		Fig. 3, Curve 2.

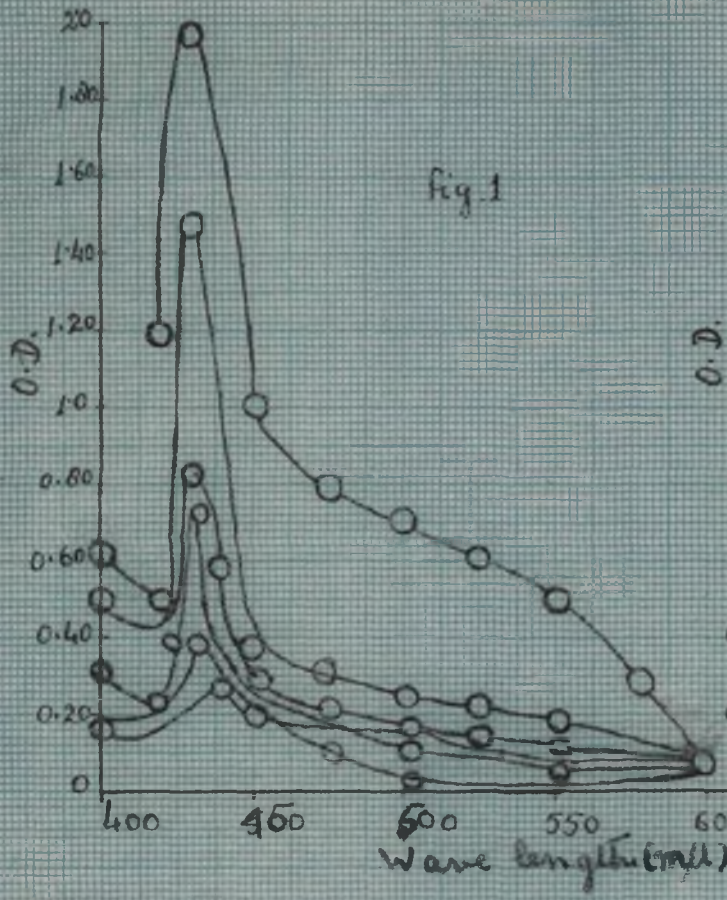


Fig. 1

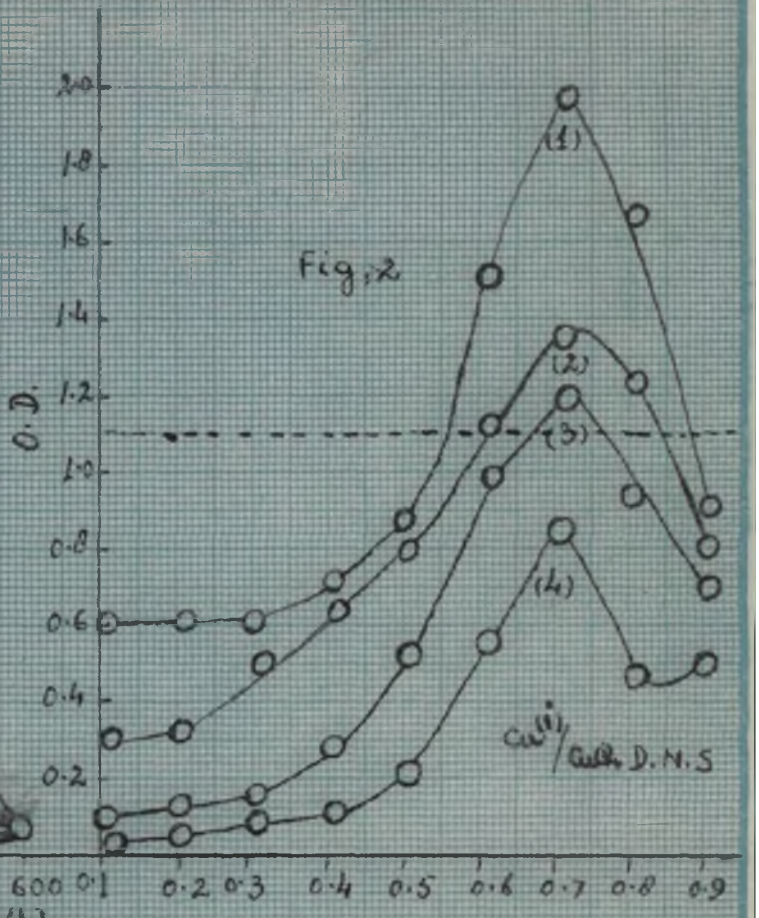


Fig. 2

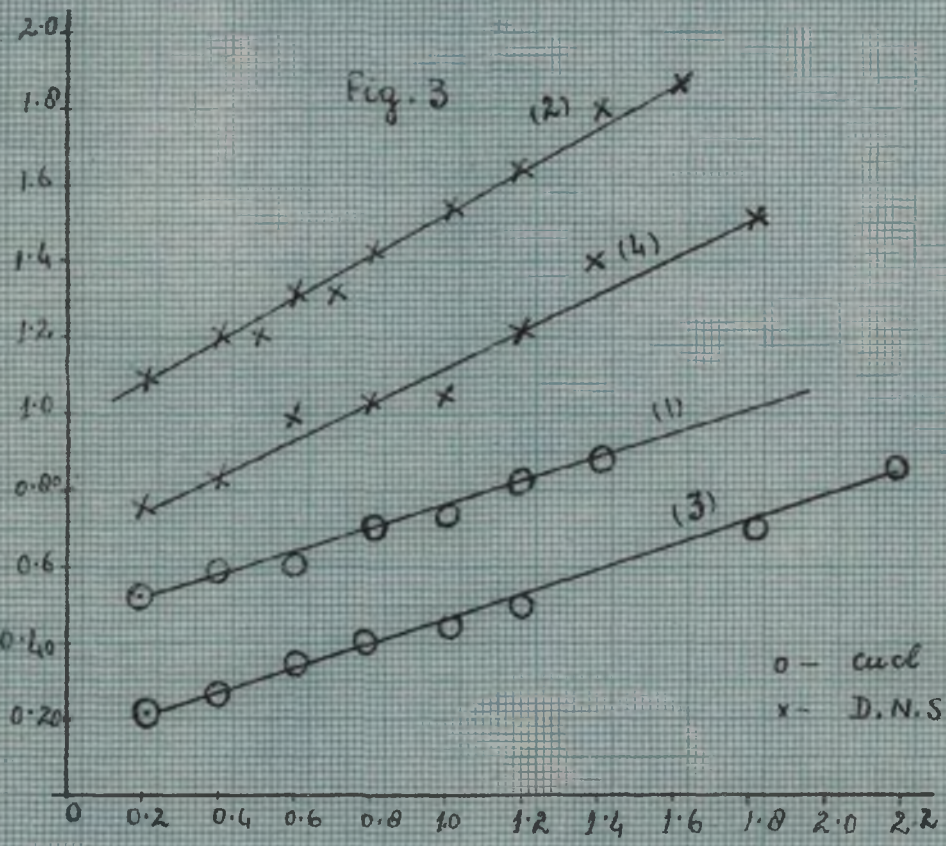


Fig. 3

Table 5.

Set No. III

Vol. of 2.5×10^{-3} M D.N.S. = 2.5 cc

Strength of CuCl = 3.3×10^{-3} M

The solutions were kpet for over six hours before the O.D. measurements.

Set No. IV

Vol. of 2.5×10^{-3} M CuCl = 2.5 cc

Strength of D.N.S. = 33×10^{-3} M

The solutions were kept for six hours before the O.D. measurements and then diluted to 10 cc

Wave length: 430 mμ

Set III		Set IV	
Vol. of CuCl	O.D.	Vol. of D.N.S.	O.D.
0.0 cc	0.10	0.0 cc	0.60
0.1 cc	0.14	0.1 cc	0.74
0.2 cc	0.18	0.2 cc	0.74
0.3 cc	0.20	0.3 cc	0.80
0.4 cc	0.26	0.4 cc	0.86
0.6 cc	0.36	0.6 cc	0.94
0.8 cc	0.40	0.8 cc	1.10
1.0 cc	0.44	1.0 cc	1.20
1.2 cc	0.50	1.2 cc	1.20
1.4 cc	0.50	1.4 cc	1.40
	Fig. 3, Curve 3.		Fig. 3, Curve 4.

The composition of the complex was also determined by the modified slop ratio method, suggested by B.S.V.R. Rao while studying the uranyl complexes of Alazarin Red S.

The absorbances of the solutions (Table 4) were plotted against the concentration of the variable components from either end of the x-axis. Curve 1 and 2 The point of intersection of the two curves corresponds to the composition of the complex assuming that only one complex is formed. The result of such a plot is given in fig. 4.

Formation constant of the complex:[27]

The calculation of stability constant of metal complexes by an optical method based on Beer' law usually, though not necessarily require prior knowledge or an assumption concerning the formula of the complex being investigated. The formula of the complex, for this purpose, is usually determined by employing the method of continuous variation.

The optical density of the solution is used to determine the relative concentrations of one of the components (usually the complex) involved in equilibrium. This involves the assumption that only one substance is appreciably coloured or that the interference from other coloured materials may be over come by applying a correction, and that Beer's law holds for the coloured substance being measured.

Let us consider the simple equilibrium

$$M + Ke \rightleftharpoons M.Ke \qquad (1)$$

for which the complex MKe is the only substance absorbing in the wave length region being used for the measurement.

We may write $$K = \frac{(MKe)}{(M)\ (Ke)} \qquad (2)$$

If X is the optical density of a solution and if Beer's law is assumed to hold for MKe, it follows that for constant length of light path

$$(MKe) = KX \qquad (3)$$

where K is the constant of proportionality. The constant may be determined by suitable optical methods. Two common methods are given below.

1. For a second solution having equal optical density but different concentrations of metal and complexing agent

$$(MKe) = KX_2 \qquad (4)$$

Since $X_1 = X_2$ $(MKe)_1$, $= (MKe)_2 = (MKe)$

Therefore we may write

$$K = \frac{(M\,Ke)}{\left[(C_M-(MKe)\right]\ \left[C\,Ke - (MKe)\right]}$$

$$= \frac{(M\,Ke)}{\left[(C_{M_2}-(MKe)\right]\ \left[CK_{e_2}-(MKe)\right]} \qquad (5)$$

where C_{M_1}, C_{M_2} = total concentrations of free and combined metal species in solution 1 and 2; and

$C_{K_{e_1}}$, $C_{K_{e_2}}$ = total concentrations of free and combined metal complexing agent species in solution 1 and 2.

Since the values of C_M and C_{K_e} in the experimental solutions are known, the above equation may be solved for (MK_e) and K.

2. An other method for determination of K involves an optical measurement of the chelate in the presence of a large excess of one of the reagents so that formation of the chelate or complex may be considered to be complete. In order to this it is necessary that the reagent in excess have not even a weak absorbance band at the wave length used. The extinction coefficent for the colored complex may then be calculated from Beer's law. Measurement of O.D. are then made at concentrations of the reagent such that the formation of the complex is incomplete and the concentration of the complex is calculated directly from Beer's law. If the formula of the complex is known, the concentration of free metal ion and of complexing agent may be determined and K may be calculated.

Turner and Anderson[28] investigated the complexes of Cu (ii) with sulphosalicylic acid and calculated the values of formation constant for 1:1 complex by employing both the methods described above. The equilibrium constant (the reciprocal of th formation constant,) reported from both the methods agreed quite well.

The formation constant of the complex in our case, was calculated as follows:

Consider the reaction

$$2\ Cu\ A + D.N.S. \rightleftharpoons Cu_2\ (D.N.S.)$$

If x represents the complex concentration at equilibrium and a and b the concentrations initially present of the metal ion and complexing agent respectively, the formation constant is given by $K = x / (a-2x)(b-x)$

Taking two values of a and b showing the same absorbance i.e. the same value of x we have

$$K = \frac{x}{(a-2x)^2(b_1-x)} = \frac{x}{(a-2x)^2(b_2-x)}$$

$$\text{Or } x = ((a_2-a_1)^2 - 4(a_2b_2-a_1b_1)) \pm \sqrt{((a_2-a_1)^2 - 4(a_2b_2-a_1b}$$

$$- 16(a_2^2b_2 - a_1^2 b_1)((b_2 - a_2) - (a_1 - b_1)) /$$

$$8((b_2 - a_2) - (a_1 - b_1))$$

For determining the value of the formation constant, the O.D., readings recorded during the continuous variation measurements were utilized. Following sets of observations were used for calculating the value of formation constant.

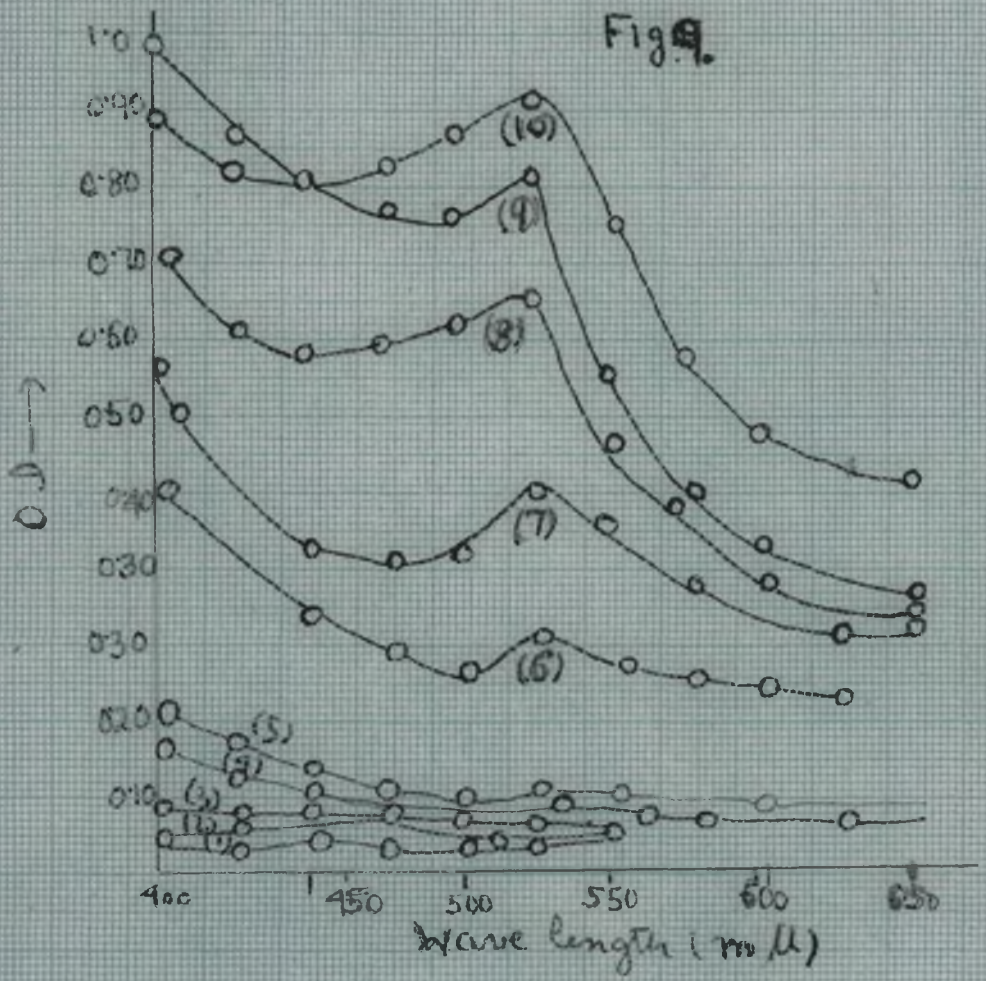
O.D. of the mixtures = 1.1

Set No. I. Conc. of CuCl (a_1) = $8.3 \times 2 \times 10^{-3}$M, Conc. of DNS ($b_1$) = $1.7 \times 2 \times 10^{-3}$M

Set No. II. Conc. of CuCl (a_2) = $7.5 \times 1.25 \times 10^{-3}$M Conc. of DNS ($b_2$) = $2.5 \times 1.25 \times 10^{-3}$M.

The absorbances of the mixtures of CuCl and DNS at

Fig 9.


1·0
0·90
0·80
0·70
0·60
0·50
0·40
0·30
0·20
0·10
O.D.
(10)
(9)
(8)
(7)
(6)
(5)
(4)
(3)
(2)
(1)
400
450
500
550
600
650
Wave length (mμ)

different pH (4.5 to 7) were measured and the effect of pH on the absorption was quantitatively studied.

Equimolecular solutions of cuprous chloride and DNS of concentration 1 x 10^{-2}M were prepared. Six samples of the complex having total volume 1.0 cc (in the ratio of Cu^{+} to DNS as 2 : 1) were prepared and then diluted to ten times by the Walpole acetate buffers of the range 4.5 to 6.50. The pH of the diluted samples were then measured with the help of Beckman pH meter (model G) with glass electrodes of general utility and the solutions were then kept for over six hours to ensure complet reaction. The optical densities of the mixtures were noted in the wave length range of 400 to 600 mu.

Table 6.

Total concentration of the complex = 1 x 10^{-3}M

Wave length mu	pH = 4.6 O.D.	pH= 5.1 O.D.	pH = 5.5 O.D.	pH = 6.0 O.D.	pH = 6.5 O.D.	pH = 7.0 O.D.
400	0.08	0.08	0.20	0.36	0.60	0.80
420	-	0.01	0.10	0.56	0.76	0.90
430	0.04	0.30	0.48	0.78	0.88	1.0
450	0.02	0.08	0.26	0.44	0.70	0.80
475	0.02	0.04	0.08	0.18	0.40	0.48
500	0.02	0.04	0.08	0.10	0.42	0.46
525	0.02	0.08	0.10	0.14	0.40	0.44
550	0.02	0.10	0.14	0.20	0.26	0.30
575	0.04	0.04	0.10	0.26	0.26	0.30
600	-	0.02	0.04	0.08	0.30	0.30

Fig. 5. Curve 1, 2, 3, 4, 5 and 6.

Spectrophotometric studies on Cu(ii) - chromotropic acid (sodium salt) Complex.

Like Cu(i) chromotropic acid reaction, the reaction between cupric chloride and chromotropic acid was also found to be a slow one and took considerable time for completion depending upon the concentration and the pH of the reaction mixtures. Thus it took two to three hours for completion in the concentration range 2.5×10^{-3} M to 5×10^{-4} M. With more dilute solutions the time for completion increased considerably and some time it took twelve hours for the red colour to develop.

In order to determine the number of complexes formed by the interaction of cupric chloride and DNS, the method of Vosburgh and Cooper was followed.

Equimolar solutions of the reactants (cupric chloride and DNS) of concentration 1×10^{-3} were mixed in the following order and the O.D. were measured in the wave length range of 400 mu to 650 mu.

Ratio	2 : 8	3 : 7	4 : 6	5 : 5	6 : 4
Cu^{++}	2 cc	3 cc	4 cc	5 cc	6 cc
D.N.S.	8 cc	7 cc	6 cc	5 cc	4 cc

Before performing the O.D. measurements, the reaction mixtures were kept for over two hours for completion of the reaction (indicated by the appearance of red colour in the solutions).

The O.D. measurements were carried out with Beckman D.U. Spectrophotometer with 1 cm corex cells and a tungsten lamp as the light source.

Table 7.

Set I. Concentration of $CuCl_2$ = 1×10^{-3} M

Concentration of D.N.S. = 1×10^{-3} M

O.D. was measured after keeping the mixtures for over two hours.

Wavelength mu	Ratio of Cupric Chloride to D.N.S.				
	2 : 8	3 : 7	4 : 6	5 : 5	6 : 4
400	0.310	0.140	0.195	0.20	0.230
410	0.310	0.145	0.190	0.210	0.235
420	0.30	0.155	0.20	0.220	0.245
430	0.30	0.165	0.210	0.235	0.260
440	0.30	0.175	0.220	0.25	0.270
450	0.30	0.185	0.230	0.265	0.285
460	0.30	0.190	0.245	0.280	0.295
475	0.32	0.20	0.265	0.315	0.330
480	0.33	0.210	0.290	0.335	0.360
490	0.33	0.225	0.310	0.345	0.375
500	0.34	0.230	0.340	0.385	0.410
525	0.370	0.255	0.405	0.430	0.450
530	0.360	0.25	0.395	0.425	0.44
535	0.365	0.240	0.390	0.415	0.430
550	0.325	0.215	0.375	0.365	0.395
575	0.240	0.150	0.255	0.245	0.275
600	0.135	0.070	0.155	0.20	0.230
625	0.090	0.040	0.090	0.130	0.150
650	0.070	0.025	0.060	0.075	0.090

Fig. 6; Curve 1, 2, 3, 4 and 5.

Absorption experiments carried out in the range 400 mu to 650 mu showed one maxima at 525 mu for the Cu(ii) - D.N.S. complex.

For determining the composition of the complex formed between cupric chloride and chromotropic and (Na salt), Job's method of continuous variation was employed. The following sets of mixture were prepared.

Set I. 0.5 cc, 1.0 cc, 1.5 cc, 2.0 cc, 2.5 cc, 3.0 cc, 3.5 cc, 4.0 cc, and 4.5 cc of $CuCl_2$ were mixed with 4.5 cc, 4.0cc, 3.5 cc, 3.0 cc, 2.5 cc, 2.0 cc, 1.5 cc, 1.0 cc and 0.5 cc of DNS respectively. The concentration of both the reactants was 1.66×10^{-3}M. Before carrying out the absorption experiments, the solutions were kept for nearly two hours to make the reaction complete.

Set II. Concentration of the reactants being 1.25×10^{-3}M and the reaction mixtures were kept for over two hour to ensure complete reaction. All other detail being the same as in Set I.

Set III. Concentration of the reactant = 1.0×10^{-3}M and the optical density measurements were performed after keeping the reaction mixtures for about three hours.

The absorbances of the reactants e.g. $CuCl_2$ and DNS were found to be negligible in this concentration range and at the wave length 525 mu.

Curves were plotted between the O.D. of the mixtures and the ratio $\frac{Cu^{+2}}{Cu^{+2} + DNS}$ at 525 mu.

Table 8.

Wave length mu

Set No. I.

Vol. of $CuCl_2$	Vol. of DNS	O.D. of the mixture
0.5 cc	4.5 cc	0.07
1.0 cc	4.0 cc	0.22
1.5 cc	3.5 cc	0.60
2.0 cc	3.0 cc	1.30
2.5 cc	2.5 cc	1.60
3.0 cc	2.0 cc	1.40
3.5 cc	1.5 cc	1.10
4.0 cc	1.0 cc	0.80
4.5 cc	0.5 cc	0.57

Set No. II.

Vol. of $CuCl_2$	Vol. of D.N.S.	O.D. of the mixture
0.5 cc	4.5 cc	0
1.0 cc	4.0 cc	0.16
1.5 cc	3.5 cc	0.46
2.0 cc	3.0 cc	1.0
2.5 cc	2.5 cc	1.40
3.0 cc	2.0 cc	1.26
3.5 cc	1.5 cc	1.0
4.0 cc	1.0 cc	0.70
4.5 cc	0.5 cc	0.38

Set No. III.

Vol. of $CuCl_2$	Vol. of D.N.S.	O.D. of mixture
0.5 cc	4.5 cc	0
1.0 cc	4.0 cc	0.10
1.5 cc	3.5 cc	0.40
2.0 cc	3.0 cc	0.74
2.5 cc	2.5 cc	1.1
3.0 cc	2.0 cc	0.76
3.5 cc	1.5 cc	0.32
4.0 cc	1.0 cc	0.08
4.5 cc	0.5 cc	0.02

Fig. 7, Curve No. (1), (2), (3).

The composition of $CuCl_2$- D.N.S. complex was furthur investigated by carrying out slope ratio method.

The results are as follows:

Table 9.

Set I. Vol. of $1x10^{-2}$M D.N.S. = 1 cc

Strength of $CuCl_2$ = $5x10^{-3}$M

Mixtures were kept for two hours.

Each mixture was diluted after completion of the reaction - 5 cc

Set II. Vol. of $1x10^{-2}$M $CuCl_2$ = 1 cc

Strength of D.N.S. = $5x10^{-3}$M

Mixtures were kept for about two hours.

Each mixture was diluted after completion of the reaction = 5 cc

Wave length: 525 mu

Set No. I.		Set No. II.	
Vol. of $CuCl_2$	O.D.	Vol. of D.N.S.	O.D.
0 cc	0.060	0 cc	0.10
0.1 cc	0.060	0.1 cc	0.10
0.2 cc	0.070	0.2 cc	0.130
0.5 cc	0.10	0.5 cc	0.140
1.0 cc	0.110	1.0 cc	0.170
1.2 cc	0.130	1.2 cc	0.175
1.4 cc	0.140	1.4 cc	0.190
1.5 cc	0.145	1.5 cc	0.20
2.0 cc	0.170	2.0 cc	0.220
2.5 cc	0.220	2.5 cc	0.25
3.0 cc	0.240	3.0 cc	0.275
3.5 cc	0.410	3.5 cc	0.280

Fig., 8, Curve 1. Fig. 8, Curve 2.

Fig. 6

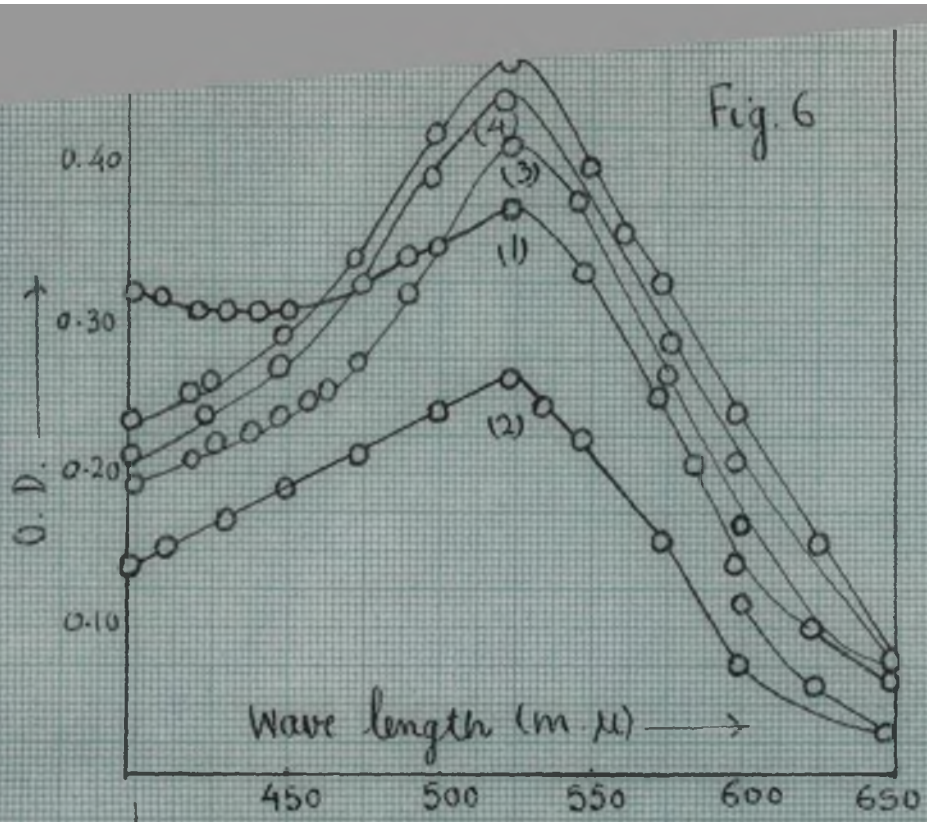


Fig. 7

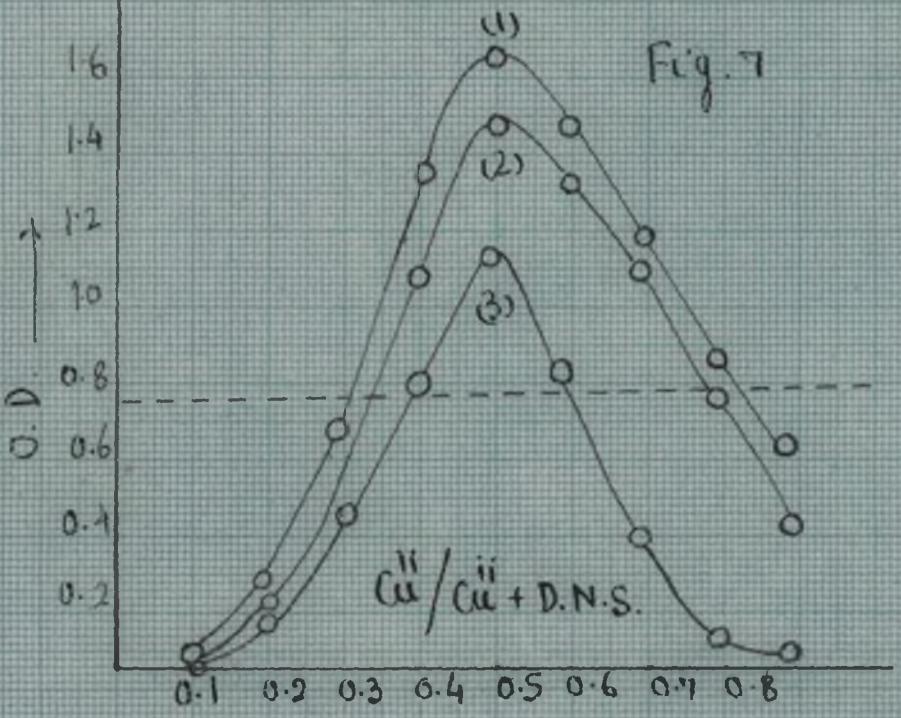
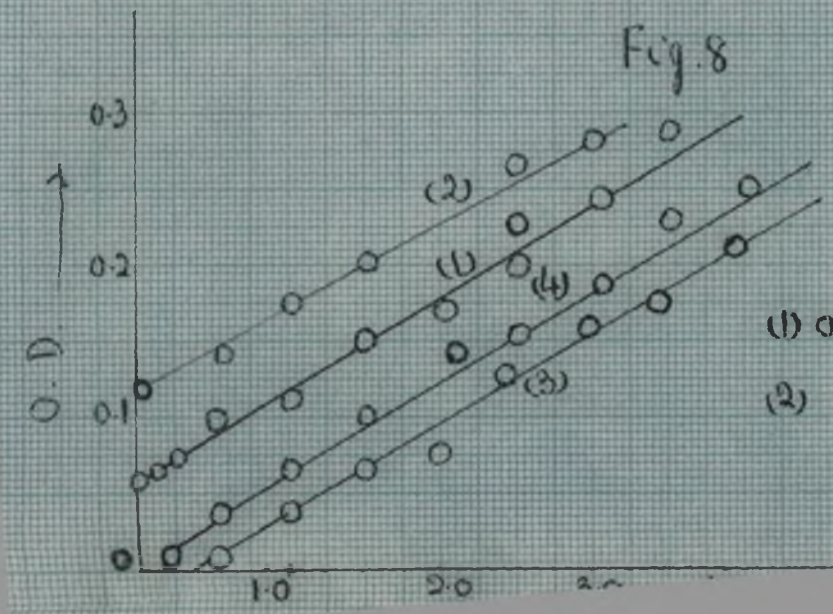


Fig. 8



(1) and (3) $CuCl_2$ added

(2) & (4) D.N.S. added

Table 9.

Set No. III. Vol. of $5x10^{-2}$M D.N.S. = 1 cc

Strength of $CuCl_2$ = $2.5x10^{-3}$M

Mixtures were kept for two hours.

Set No. IV. Vol. of $5x10^{-2}$M $CuCl_2$ = 1 cc

Strength of D.N.S. = $2.5x10^{-3}$M

Mixtures were kept for over two hours.

Each mixture of the set III and IV were diluted after completion of the reaction = 5 cc.

Wave length 525 mu

Set No. III.		Set No. IV.	
Vol. of $CuCl_2$	O.D.	Vol. of D.N.S.	O.D.
0. cc	-	0. cc	-
0.2 cc	0.01	0.2 cc	0.02
0.5 cc	0.01	0.5 cc	0.03
1.0 cc	0.04	1.0 cc	0.07
1.5 cc	0.065	1.5 cc	0.10
2.0 cc	0.075	2.0 cc	0.125
2.5 cc	0.13	2.5 cc	0.150
3.0 cc	0.16	3.0 cc	0.180
3.5 cc	0.17	3.5 cc	0.22
4.0 cc	0.20	4.0 cc	0.25

Fig. 8, Curve (3) Fig. 8, Curve (4)

In order to study the influence of pH on the absorbance maxima, equimolecular solutions of the reactants of concentration $1x10^{-2}$M were prepared in the ratio of 1:1 (total voloume 1.0 cc) and diluted with buffers of the pH range 2.5 to 11.0 (employing citric acid - NaoH buffer for pH range 2.5 to 3.5; Walpole acetic acid buffer for the range 3.5 to 6.0, and phosphate buffers for 6.0 to 11.0) to 10 cc.

The solutions were kept for three hours and the absorbances were noted at different wave lengths ranging from 400 mu to 650 mu.

Table 10.

Total concentration of the complex = 1.0×10^{-3} M

Wave length	pH= 3.0	pH=4.1	pH= 4.7	pH= 6.0	pH= 6.7	pH= 7.6	pH= 8.6	pH= 9.0	pH= 9.5	pH=1.0
	O.D.	O.D.	O.D.	O.D.	O.D.	O.D.	O.D.	O.D.	O.D.	O.D.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
400	0.07	0.10	0.035	0.010	0.17	0.20	0.50	0.66	0.80	1.0
425	0.06	0.065	0.055	0.015	0.12	0.17	0.41	0.50	0.71	0.92
450	0.04	0.045	0.020	0.010	0.10	0.14	0.34	0.43	0.68	0.90
475	0.035	0.025	0.025	0.010	0.09	0.10	0.29	0.40	0.69	0.92
500	0.025	0.025	0.025	-	0.09	0.09	0.25	0.40	0.71	0.95
525	-	0.020	-	-	0.10	0.12	0.30	0.50	0.75	1.0
550	-	0.020	-	-	0.08	0.10	0.26	0.45	0.56	0.83
575	-	-	-	-	0.08	0.08	0.24	0.36	0.47	0.66
600	-	-	-	-	0.07	0.08	0.22	0.32	0.36	0.56
625	-	-	-	-	0.07	0.07	0.21	0.30	0.33	0.52
650	-	-	-	-	0.05	0.06	0.20	0.30	0.30	0.50

Fig. 9, Curve (1),(2),(3),(4),(5),(6),(7),(8),(9) and (10).

(Figures facing page 40a)

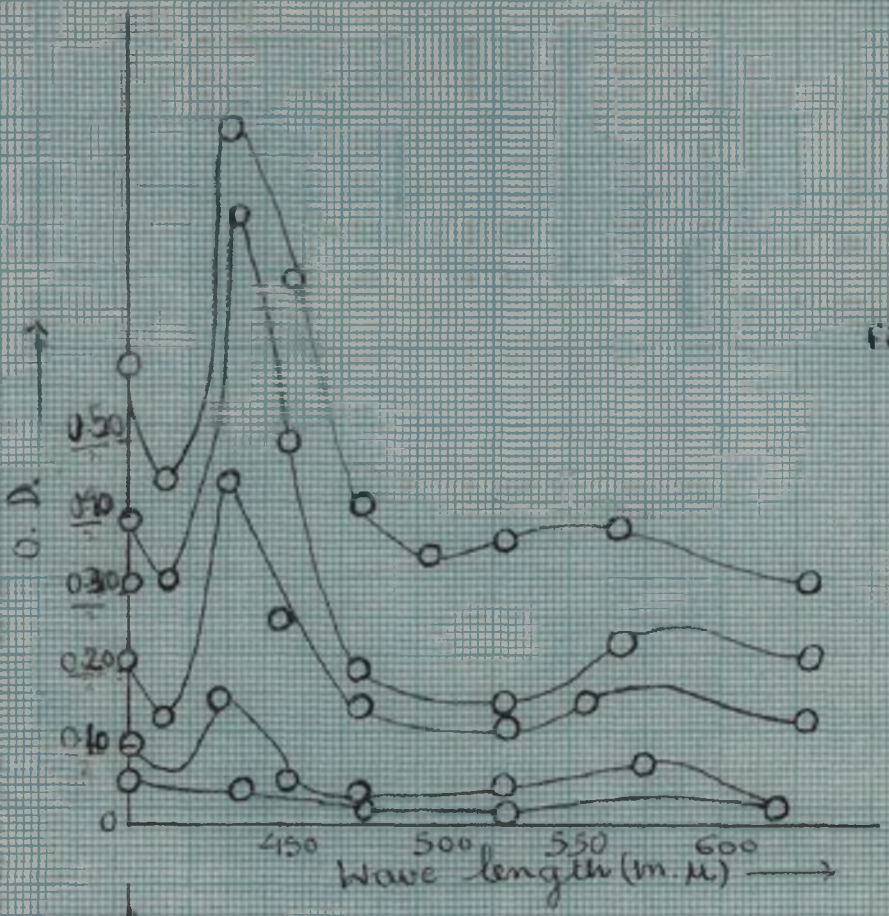


Fig. 5

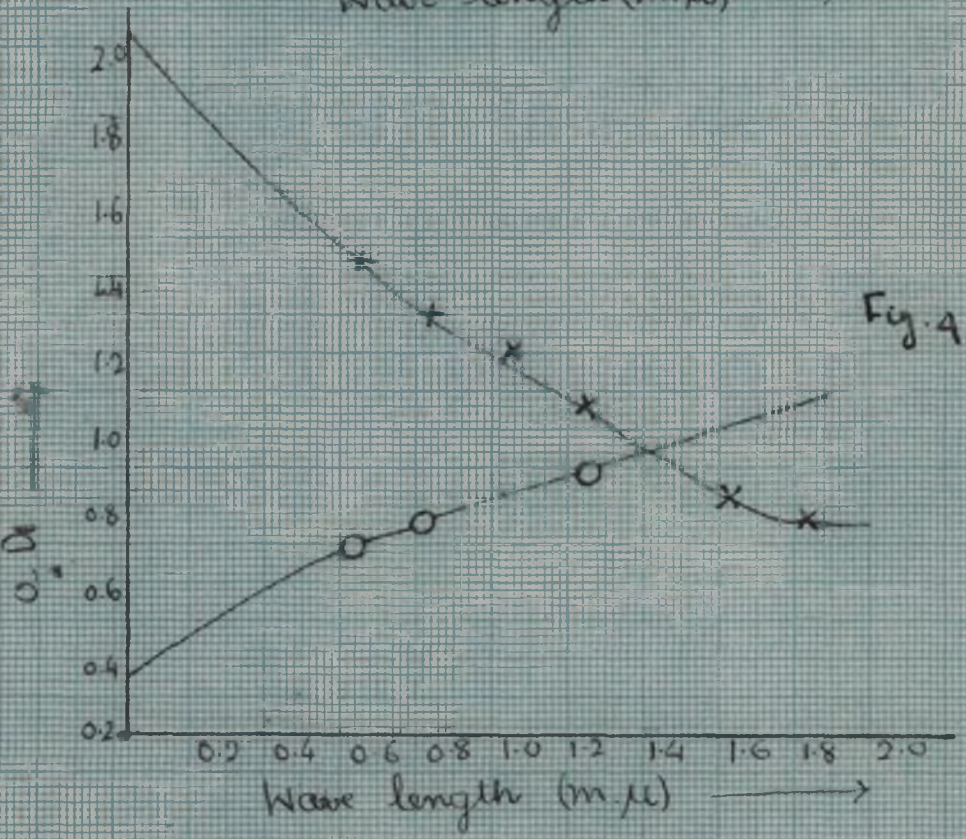


Fig. 4

The formation constant and free energy was calculated as follows:

For the reaction $mA + nB \rightleftharpoons A_m B_n$

where $m/n = 1$ or $m=n=1$; $K = \frac{x}{(a-x)(b-x)}$

(where x is the concentration of the complex, and a and b are the initial concentrations of cupric chloride and D.N.S. respectively). Taking two concentration a, and a_2, and b, and b_2 of the reactants giving the same optical density.

$$K = \frac{x}{(a_1-x)(b_1-x)} = \frac{x}{(a_2-x)(b_2-x)}$$

Knowing the value of x from the above equation, K is calculated from different values of a and b.

The values of a_1, b_1, a_2, b_2 and x were determined from the figure of Job's method of continuous variation, used for the composition of Cu (ii)-D.N.S. complex (Fig. 7, Curve (1),(2) and (3) wide Table No. 8.) and the values are given as follows:

Values of a_1 and b_1 are $3.1 \times 166 \times 10^{-3}$ M and $6.9 \times 1.66 \times 10^{-3}$ M and that of a_2 and b_2 $3.6 \times 1.25 \times 10^{-3}$ M and $6.4 \times 1.25 \times 10^{-3}$ M respectively at the O.D (0.70).

Spectrophotometric studies on Mn(iii) - Chromotropic acid (sodium salt) complex:

In order to determine the number of complexes formed by the interaction of Mn(iii) SO_4 and DNS, the method of Vosburgh and Cooper was employed. Equimolar solutions of the reactants of concentration 1 x 10^{-2}M were mixed in the ratio of Mn(iii) to DNS as 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 by mixing 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 cc of manganic sulphate to 8.0, 7.0, 6.0, 5.0, 4.0 and 3.0 cc of D.N. S and respectively their optical density were measured in the wave length range of 350 to 600 mu. Also, Mn(iii) sulphate of concentration 1 x 10^{-2}M was mixed with dil. H_2SO_4 so that the mixtures in the ratio of Mn(iii) to dil H_2SO_4 as 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 were obtained and their optical density were also measured in the wave length range of 350 to 600 mu.

The O.D. measurements were performed with Busch and Lomb 'Spectronic 20' after giving sufficient warming up period to the apparatus.

Table 11.

Set I. Concentration of Mn(iii) sulphate = 1×10^{-2}M

Concentration of D.N.S. = 1×10^{-2}M

Wavelength mu	Ratio of Mn(iii) sulphate to D.N.S. 2:8	3:7	4:6	5:5	6:4	7:3
350	1.30	1.20	1.20	1.20	1.1	1.5
360	1.20	1.10	1.10	1.10	1.1	1.40
370	0.52	0.61	0.90	0.95	1.0	1.30
380	0.25	0.39	0.52	0.60	0.80	0.90
390	0.190	0.34	0.42	0.50	0.70	0.80
400	0.180	0.37	0.49	0.51	0.75	0.88
410	0.21	0.44	0.50	0.56	0.90	0.95
420	0.22	0.49	0.53	0.59	0.95	1.0
430	0.21	0.44	0.56	0.60	0.90	1.1
440	0.20	0.46	0.54	0.58	0.88	1.1
450	0.20	0.39	0.50	0.54	0.85	0.90
475	0.14	0.27	0.37	0.40	0.62	0.69
500	0.08	0.15	0.21	0.22	0.36	0.37
525	0.03	0.07	0.11	0.13	0.14	0.19
550	0.02	0.05	0.07	0.09	0.07	0.12
575	0.01	0.03	0.04	0.08	0.03	0.05
600	0.01	0.04	0.03	0.07	0.02	0.01

Fig. 10, Curve 1, 2, 3, 4, 5 and 6.

Table 12.

Set II. Strength of Mn(iii) SO_4 solution = 1 x 10^{-2}M

Wave length mu	Ratio of Mn(iii) sulphate to dil H_2SO_4 2:8	3:7	4:6	5:5	6:4
350	0.18	0.21	0.28	0.37	0.45
360	0.15	0.20	0.22	0.325	0.36
370	0.11	0.15	0.17	0.245	0.34
380	0.10	0.12	0.14	0.19	0.25
390	0.075	0.105	0.12	0.135	0.18
400	0.05	0.075	0.09	0.125	0.125
410	0.04	0.06	0.07	0.09	0.11
420	0.03	0.04	0.06	0.09	0.11
430	0.015	0.04	0.06	0.10	0.12
440	0.110	0.045	0.075	0.11	0.13
450	0.010	0.05	0.075	0.125	0.15
475	0.03	0.075	0.09	0.15	0.20
500	0.05	0.09	0.11	0.175	0.24
515	0.11	0.10	0.12	0.180	0.25
525	0.08	0.09	0.11	0.14	0.20
550	0.02	0.04	0.07	0.09	0.12

Fig. 11, Curve 1, 2, 3, 4 and 5.

Absorption experiments carried out in the range 350 to 600 mu show λ_{max} of the complex was found to be at 430 mu whereas the Mn(iii) showed a single absorption peak at 515 mu.

The composition of the Mn(iii) - DNS complex was determined by Job's method of continuous variation. The following sets of mixtures were prepared:

Set No. 1. 0.5 cc, 1.0 cc, 1.5 cc, 2.0 cc, 2.5 cc, 3.0 cc, 4.0 cc and 4.5 cc of Mn(iii) SO_4 were mixed with 4.5 cc,

4.0 cc, 3.5 cc, 3.0 cc, 2.5 cc, 2.0 cc, 1.5 cc, 1.0 cc and 0.5 cc of D.N.S. respectively. The concentration of both the reactants was 2.5×10^{-3}M.

Set. II. Concentration of the reactants being 1.66×10^{-3}M, all other details being the same as in Set I.

Set III. Concentration of the reactants = 1.25×10^{-3}M and all other details being the same as in Set I.

Set IV. Concentration of the reactant = 1.0×10^{-3}M and other details being the same as in Set I.

The absorbances of the reactants e.g., Mn(iii) SO_4 and D.N.S. were found to be negligible in this concentration range.

Curves were plotted between the O.D. of the mixtures and the ratio Mn(iii)/Mn^{iii} + D.N.S. at 430 mu.

Table 13.

Wave length : 430 mu.

Set I.

Vol. of $Mn^{iii}SO_4$	Vol. of D.N.S.	O.D. of the mixtures
0.5 cc	4.5 cc	0.6
1.0 cc	4.0 cc	0.10
1.5 cc	3.5 cc	0.15
2.0 cc	3.0 cc	0.25
2.5 cc	2.5 cc	0.45
3.0 cc	2.0 cc	0.41
3.5 cc	1.5 cc	0.50
4.0 cc	1.0 cc	0.71
4.5 cc	0.5 cc	1.10

Fig. 12, Curve 1.

Set II.

Vol. of $Mn^{iii}SO_4$	Vol. of D.N.S.	O.D. of the mixtures.
0.5 cc	4.5 cc	0.03
1.0 cc	4.0 cc	0.08
1,5 cc	3.5 cc	0.12
2.0 cc	3.0 cc	0.14
2.5 cc	2.5 cc	0.34
3.0 cc	2.0 cc	0.32
3.5 cc	1.5 cc	0.36
4.0 cc	1.0 cc	0.53
4.5 cc	0.5 cc	0.95

Fig. 12, Curve 2.

Table 14.

Wave length 430 mu

Set III.			Set IV.		
Vol. of $Mn^{iii}SO_4$	Vol. of D.N.S.	O.D. of the mixtures	Vol. of $Mn^{iii}SO_4$	Vol. of D.N.S.	O.D. of the mixtures
0.5 cc	4.5 cc	0.01	0.5 cc	4.5 cc	0
1.0 cc	4.0 cc	0.05	1.0 cc	4.0 cc	0.02
1.5 cc	3.5 cc	0.06	1.5 cc	3.5 cc	0.03
2.0 cc	3.0 cc	0.09	2.0 cc	3.0 cc	0.07
2.5 cc	2.5 cc	0.20	2.5 cc	2.5 cc	0.18
3.0 cc	2.0 cc	0.18	3.0 cc	2.0 cc	0.15
3.5 cc	1.5 cc	0.29	3.5 cc	1.5 cc	0.26
4.0 cc	1.0 cc	0.41	4.0 cc	1.0 cc	0.36
4.5 cc	0.5 cc	0.71	4.5 cc	0.5 cc	0.48

Fig. 12, Curve (3) Fig. 12, Curve (4).

The Composition of Mn^{iii}- DNS was furthur investigated by carrying out slope ratio method.

The results are given below:

Table 15.

Set I. Vol. of 2.50×10^{-3} M D.N.S. = 1 cc

Strength of Mn(iii) SO_4 = 1.66×10^{-3} M

Set II. Vol. of 2.50×10^{-3} M Mn(iii) SO_4 = 1 cc

Strength of D.N.S. = 1.66×10^{-3} M

The mixtures of the Set I and II were diluted to 5 cc.

Wave length 430 mu

Vol. of $Mn^{(iii)}SO_4$	O.D.	Vol. of D.N.S.	O.D.
0 cc	-	0 cc	-
0.2 cc	0.010	0.2 cc	-
0.5 cc	0.040	0.5 cc	-
1.0 cc	0.110	1.0 cc	0.025
1.5 cc	0.180	1.5 cc	0.150
2.0 cc	0.250	2.0 cc	0.140
2.5 cc	0.310	2.5 cc	0.160
3.0 cc	0.380	3.0 cc	0.220
		3.5 cc	0.260

Fig. 13, Curve (1) Fig. 13, Curve (2)

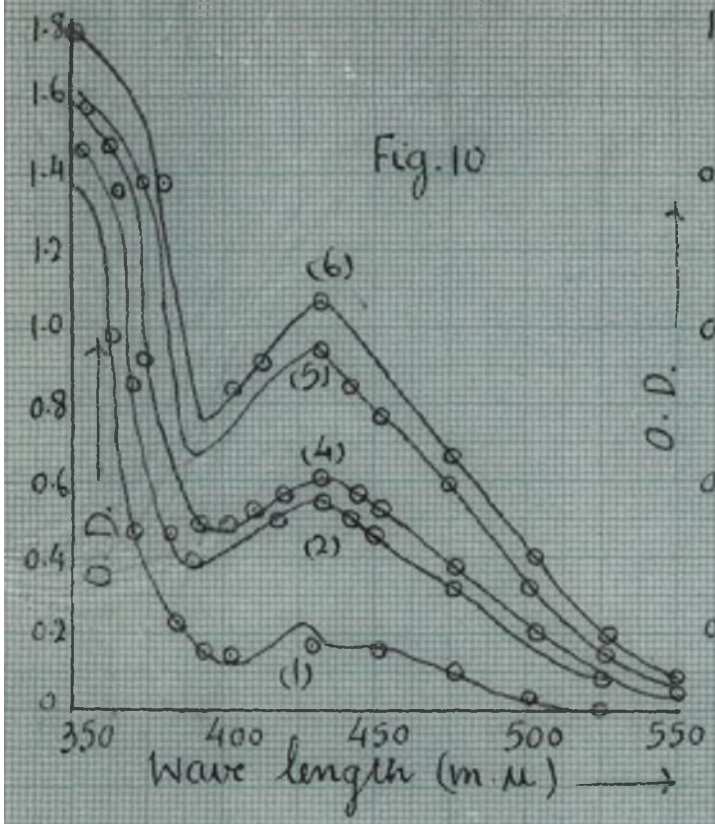


Fig. 10

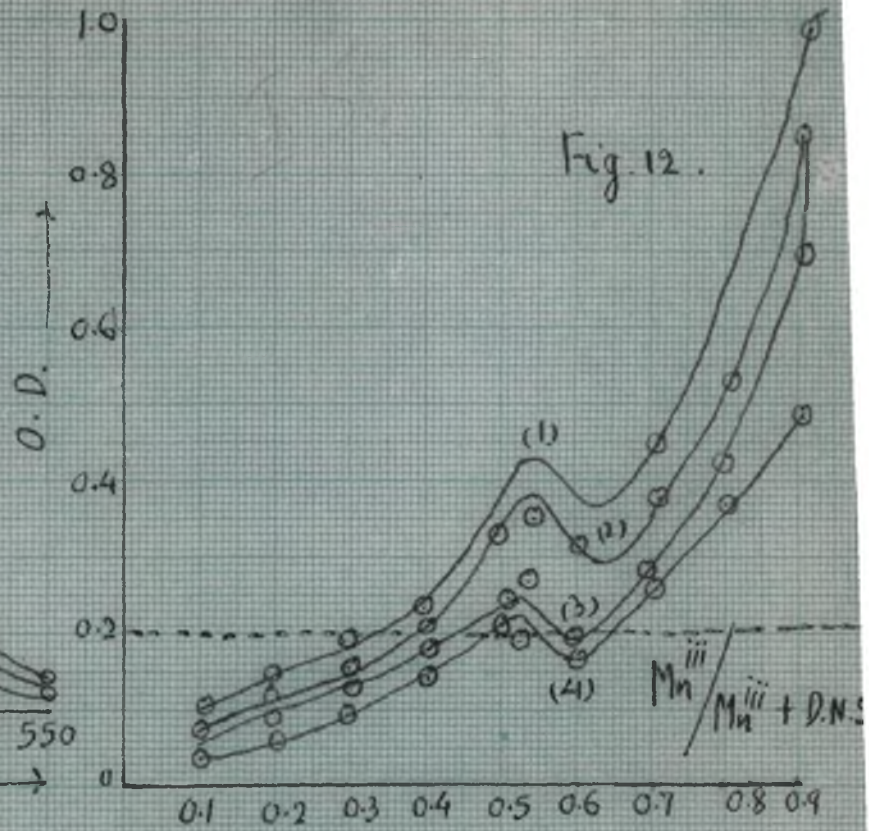


Fig. 12.

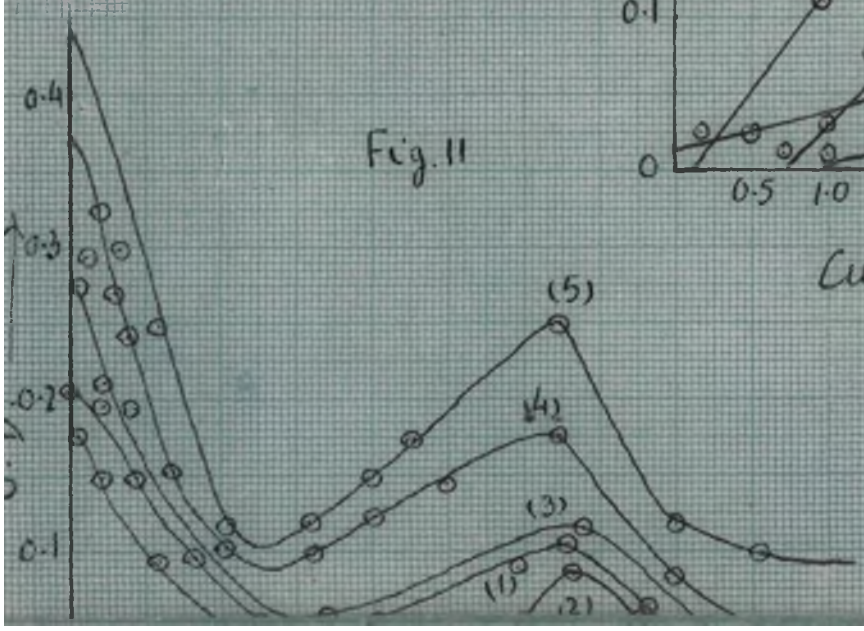


Fig. 11

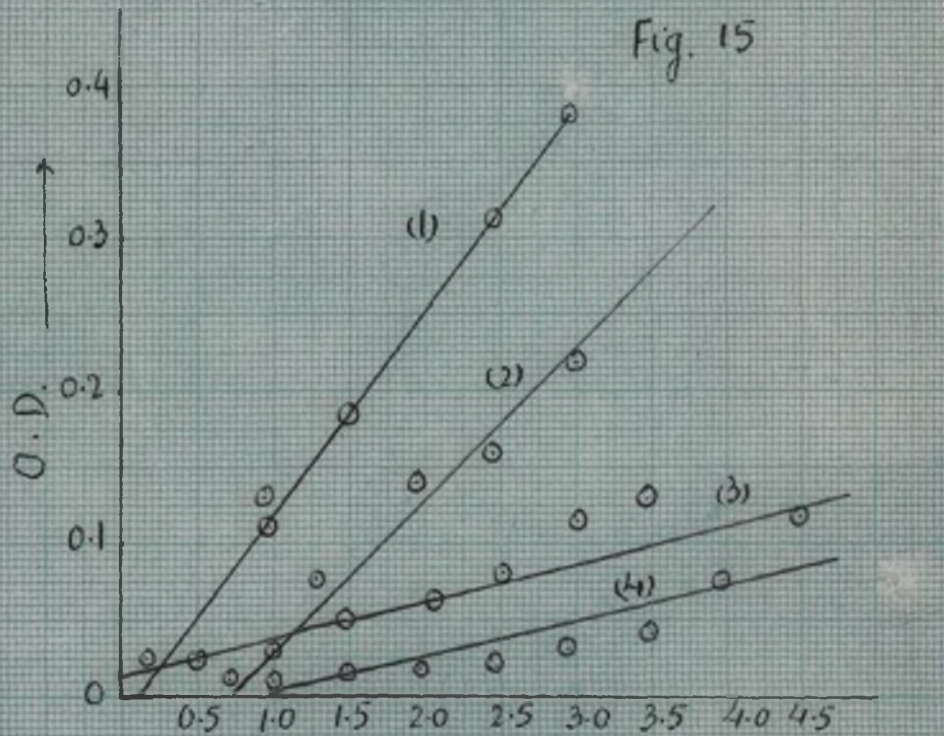


Fig. 15

Curve (1) and (3) Mn^{iii} SO_4 added

(2) " (4) D. N. S. "

Table 16.

Set III. Vol. of 1.66×10^{-3}M D.N.S. = 1 cc

Strength of Mn(iii) SO_4 = 1×10^{-3}M

Set IV. Vol. of 1.66×10^{-3}M Mn(iii) SO_4 = 1 cc

Strength of D.N.S. = 1×10^{-3}M

The mixtures of the set III and IV were diluted to 5 cc.

Wave length: 430 mu

Vol. of Mn(iii)SO_4	O.D.	Vol. of D.N.S.	O.D.
0 cc	0.01	0 cc	-
0.2 cc	0.025	0.5 cc	-
0.5 cc	0.025	1.0 cc	0.010
1.0 cc	0.050	1.5 cc	0.015
1.5 cc	0.050	2.0 cc	0.02
2.0 cc	0.060	2.5 cc	0.025
2.5 cc	0.080	3.0 cc	0.030
3.0 cc	0.120	3.5 cc	0.040
3.5 cc	0.130	4.0 cc	0.070
4.0 cc	0.150	4.5 cc	0.080

Fig. 13, Curve (3) Fig. 14, Curve (4)

The formation constant and free evergy was calculated by the method used in case of Cu (ii)– D.N.S. complex.

$$k = \frac{x}{(a_1-x)\ (b_1-x)} = \frac{x}{(a_2-x)\ (b_2-x)}$$

$$\text{or } x = \frac{a_1b_1-a_2\ b_2}{(a_1+b_1)-(a_2+b_2)}$$

where x represents the concentration of the complex at equilibrium and (a_1+b_1) and (a_2+b_2) are two concentration of the reactants being the same O.D.

For two mixtures having the same optical density (0.20) the values of a_1, a_2, b_1 and b_2 come out (from the continuous variation curves Fig. 12).

$$a_1 = 6.2\text{x}1.25\text{x}10^{-3}\text{M}, \quad b_1 = 3.8\text{x}1.25\text{x}10^{-3}\text{M}$$

$$a_2 = 6.6\text{x}1.0\text{x}10^{-3}\text{M}, \quad b_2 = 3.4\text{x}1\text{x}10^{-3}\text{M}$$

Spectrophotometric studies on V(iv)-Chromotropic acid (sodium salt

Preliminary experiments showed that the reaction between vanadyl sulphate and D.N.S. was a slow one. In the case of fairly concentrated solutions ($2.5\text{x}10^{-3}$M to $1\text{x}10^{-3}$M) it took about six hours for completion whereas with dilute solutions ($1\text{x}10^{-3}$M to $2\text{x}10^{-4}$M) the time interval was more than twelve hours.

In order to determine the number of complexes formed by the interaction of vanadyl sulphate with D.N.S., the method of Vosburgh and cooper was followed.

Equimolecular solution ($2.5x10^{-3}M$) of vanadyl sulphate and chromotropic acid (Na salt) were mixed in the ratios 2:8, 3:7, 4:6, 5:5; 6:4 and 7:3 respectively and were kept for about six hours to ensure complete reaction, their O.D. in 1 Cu corex cell were measured at different wave lengths (400 mu to 650 mu) with a D.U. Spectrophotometer (tungston lamp as the source of light).

Table 17.

Concentration of vanadyl sulphate = $2.5x10^{-3}M$

Concentration of D.N.S. = $2.5x10^{-3}M$

O.D. was measured after keeping the mixtures for over six hours.

Wavelength mu	Ratio of vanadyl sulphate to D.N.S. 2:8	3:7	4:6	5:5	6:4	7:3
400	0.2	0.40	0.80	0.80	1.0	1.10
425	0.12	0.26	0.50	0.70	0.90	1.0
450	0.10	0.18	0.40	0.54	0.94	1.1
475	0.04	0.14	0.20	0.42	0.84	1.0
500	0.02	0.12	0.20	0.34	0.70	0.80
525	0.14	0.24	0.34	0.40	0.52	0.70
550	0.10	0.16	0.30	0.36	0.54	0.58
575	0.06	0.14	0.20	0.30	0.40	0.50
600	0.04	0.10	0.18	0.30	0.32	0.38
625	0.04	0.08	0.14	0.20	0.26	0.30
650	0.04	0.06	0.16	0.20	0.22	0.30

Fig. 14, Curve (1),(2),(3),(4),(5) and (6).

Absorption experiments carried out in the range 400 mu to 650 show one maxima at 525 mu for V(iv)-D.N.S. complex.

The Job's method of continuous variation was employed to determine the composition of V (iv)- D.N.S. complex. The following sets of mixtures were prepared Set No. I.

0.5 cc, 1.0 cc, 1.5 cc, 2.0 cc, 2.5 cc, 3.0 cc, 3.5 cc, 4.0 cc and 4.5 cc of VO SO_4 were mixed with 4.5 cc, 4.0 cc, 3.5 cc, 3.0 cc, 2.5 cc, 2.0 cc, 1.5 cc, 1.0 cc and 0.5 cc of D.N.S. respectively. T he concentration of both the reactants was 2.5×10^{-3}M.

Before carrying out the absorption experiments, the solutions were kept for nearly six hours to ensure complete reaction.

Set II. Concentration of the reactants being 2.0×10^{-3}M and the reactions mixtures were kept for over six hours. All other details being the same as in Set I.

Set III. Concentration of the reactants = 1.66×10^{-3}M and the reactions mixtures were kept for over six hours.
Set IV. Concentration of the reactants = 1.25×10^{-3}M, the reaction mixtures were kpet for over six hours.

The absorbances of the reactants e.g. $VOSO_4$ and D.N.S. were found to be negligible in this concentration range and wave length (525 mu).

Curves were plotted between the O.D. of the mixtures and the ratio $\frac{VO^{++}}{VO^{++} + D.N.S.}$ at 525 mu.

Table 18.

Wave length: 525 mu

Set I.

Vol. of $VOSO_4$	Vol. of D.N.S.	O.D. of the mixtures
0.5 cc	4.5 cc	0.290
1.0 cc	4.0 cc	0.40
1.5 cc	3.5 cc	0.50
2.0 cc	3.0 cc	0.57
2.5 cc	2.5 cc	0.64
3.0 cc	2.0 cc	0.57
3.5 cc	1.5 cc	0.46
4.0 cc	1.0 cc	0.36
4.5 cc	0.5 cc	0.29

Fig.15, Curve (1)

Set II.

Vol. of $VOSO_4$	Vol. of D.N.S.	O.D. of the mixture
0.5 cc	4.5 cc	0.20
1.0 cc	4.0 cc	0.26
1.5 cc	3.5 cc	0.31
2.0 cc	3.0 cc	0.40
2.5 cc	2.5 cc	0.44
3.0 cc	2.0 cc	0.39
3.5 cc	1.5 cc	0.33
4.0 cc	1.0 cc	0.27
4.5 cc	0.5 cc	0.20

Fig. 15, Curve (2)

Table 19.

Wave length: 525 mu

Set III.

Vol. of $VOSO_4$	Vol. of D.N.S.	O.D. of the mixture
0.5 cc	4.5 cc	0.05
1.0 cc	4.0 cc	0.16
1.5 cc	3.5 cc	0.24
2.0 cc	3.0 cc	0.29
2.5 cc	2.5 cc	0.38
3.0 cc	2.0 cc	0.35
3.5 cc	1.5 cc	0.30
4.0 cc	1.0 cc	0.23
4.5 cc	0.5 cc	0.15

Fig. 15, Curve (3)

Set IV.

Vol. of $VOSO_4$	Vol. of D.N.S.	O.D.of the mixture
0.5 cc	4.5 cc	0.05
1.0 cc	4.0 cc	0.12
1.5 cc	3.5 cc	0.20
2.0 cc	3.0 cc	0.28
2.5 cc	2.5 cc	0.34
3.0 cc	2.0 cc	0.30
3.5 cc	1.5 cc	0.25
4.0 cc	1.0 cc	0.19
4.5 cc	0.5 cc	0.14

Fig. 15, Curve (4)

The composition of V(iv)-D.N.S. was furthur investigated by employing slope ratio method,

Table 20.

Set I. Vol. of $1x10^{-2}M$ DN.S. = 1.0cc

Strength of $VOSO_4$ = $5x10^{-3}M$

Mixtures were kept for six hours.

Each mixture was diluted to 5 cc after completion of the reaction.

Set II. Vol. of $1x10^{-2}M$ $VOSO_4$ = 1.0 cc

Strength of D.N.S. = $5x10^{-3}M$

Mixtures were kept for six hours and then diluted to 5 cc.

Set I.		Set II.	
Vol. of $VOSO_4$	O.D.	Vol. of D.N.S.	O.D.
.0 cc	0.53	0 cc	0.2
0.2 cc	0.62	0.2 cc	0.26
0.5 cc	0.70	0.5 cc	0.24
1.0 cc	0.88	1.0 cc	0.48
1.5 cc	1.1	1.5 cc	0.70
2.0 cc	1.20	2.0 cc	0.90
2.5 cc	-	2.5 cc	1.1
3.0 cc	-	3.0 cc	1.20
3.5 cc	-	3.5 cc	-
4.0 cc	-	4.0 cc	-

Fig. 16, Curve (1) Fig. 16, Curve (2)

Table 21.

Set III. Voloume of $2.5x10^{-3}$M D.N.S. = 1.0 cc
Strength of $VOSO_4$ = $1.25x10^{-3}$M

Set IV. Voloume of $2.5x10^{-3}$M $VOSO_4$ = 1.0 cc
Strength of D.N.S. = $1.25x10^{-3}$M

Mixtures each of the two sets were diluted to 5 cc after completion of the reaction.

Wave length: 525 mu

Set III.		Set IV.	
Vol. of $VOSO_4$	O.D.	Vol. of D.N.S.	O.D.
0 cc	0.20	0 cc	-
0.2 cc	0.24	0.2 cc	-
0.4 cc	0.30	0.4 cc	-
0.6 cc	0.37	0.6 cc	0.04
0.8 cc	0.42	0.8 cc	0.20
1.0 cc	0.48	1.0 cc	0.26
1.5 cc	0.64	1.5 cc	0.40
2.0 cc	0.78	2.0 cc	0.60
2.5 cc	1.0	2.5 cc	0.80
3.0 cc	1.20	3.0 cc	0.80
3.5 cc	1.20	3.5 cc	1.0
Fig. 17, Curve (3)		Fig. 17, Curve (4)	

The influence of PH on the formation of the complex was investigated by mixing equimolar solutions of ($1.0x10^{-2}$M) of the reactants in the ratio of 1:1 and then diluted them ten times by the buffers (Walpole pH 4 to 6.5, Di sodium and Mono sodium by drogen phosphates for pH 6.5 to 9.0 and

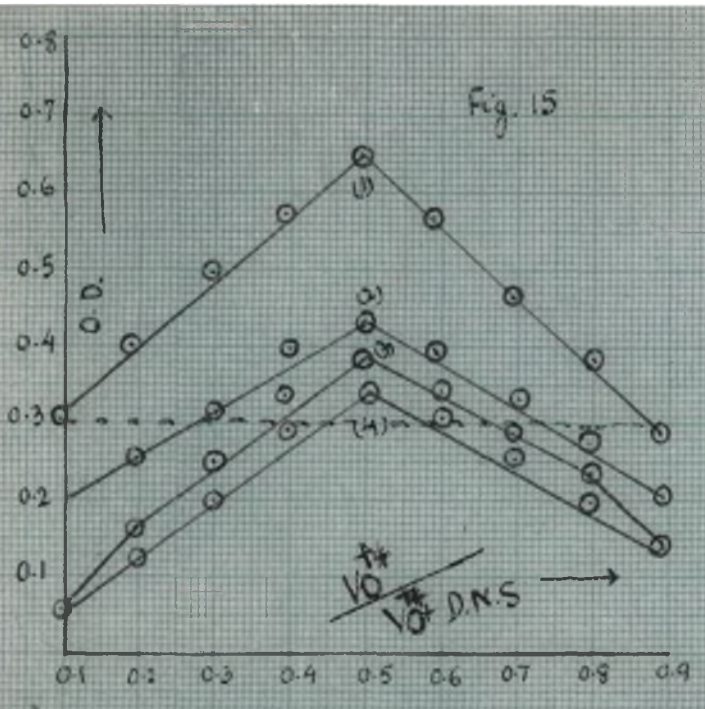


Fig. 15

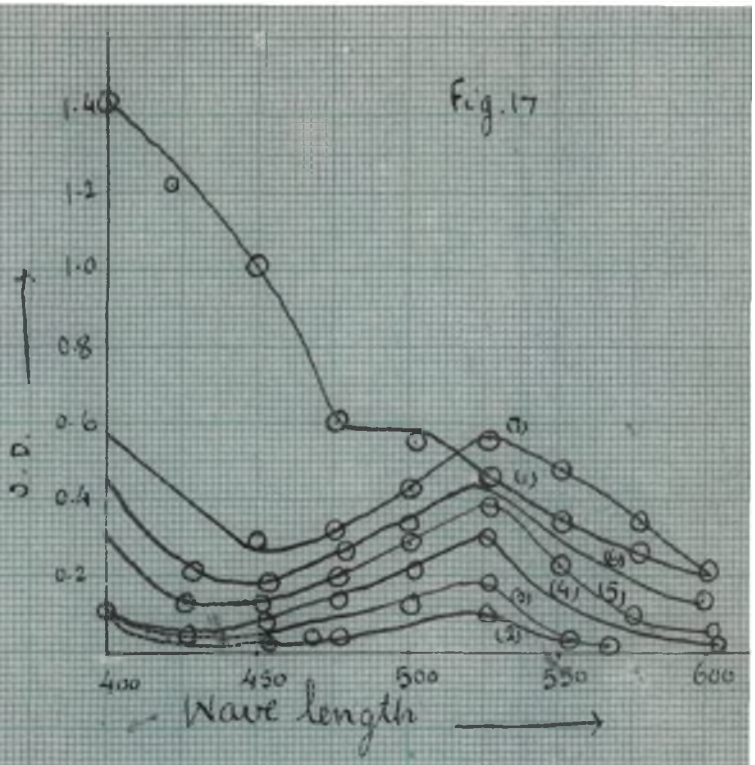
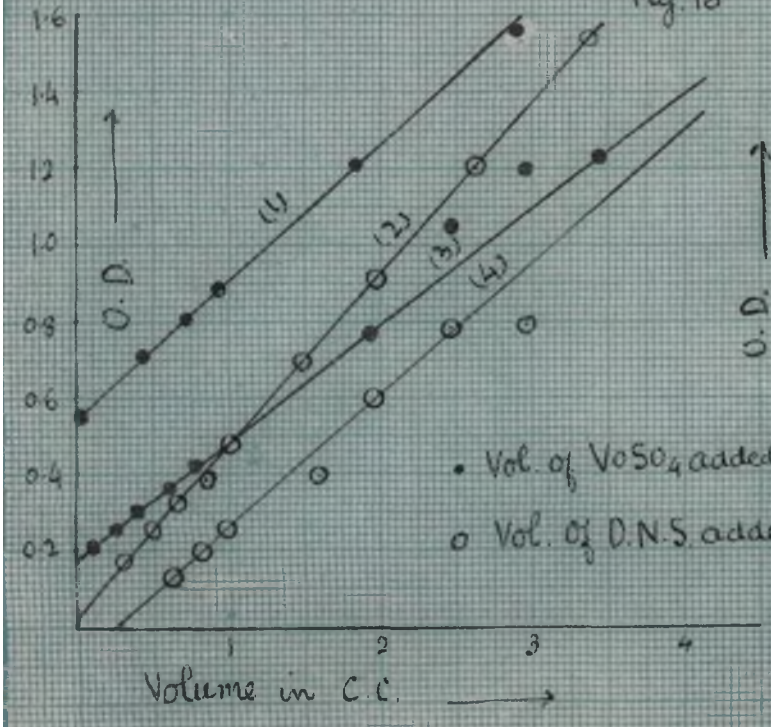


Fig. 17

Fig. 16



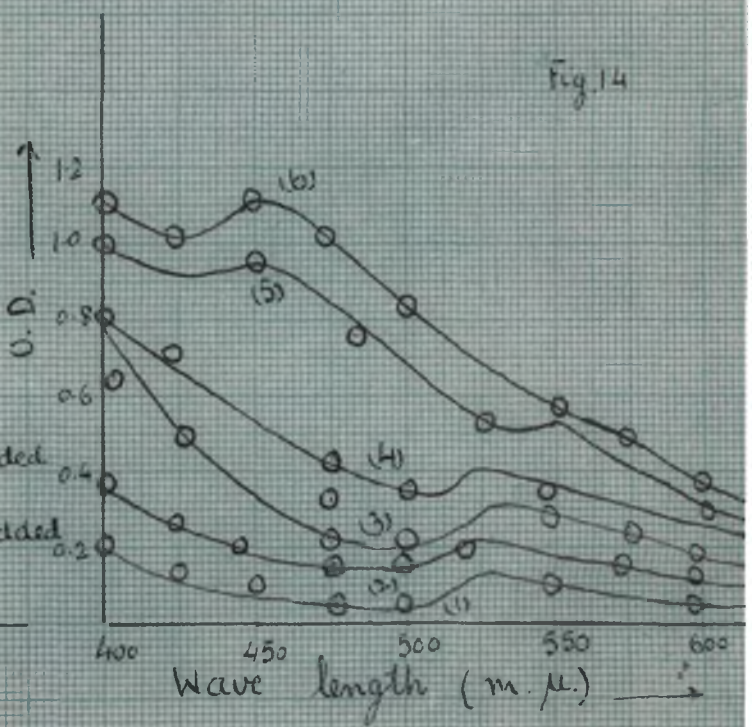


Fig. 14

Di sodium hydrogen phosphate-sodiumhydroxide pH 9.5 to 12.0), mixtures in the pH range 4 to 12 were thus obtained. The absorbances of these solutions were measured at the wave length range of 400 to 600mu.

Table 22.

Total concentration of the complex = 1.0×10^{-3} M

Wave length mU	pH= 5.0	pH= 5.6	pH= 7.1	pH=8.3	pH=9.1	pH=9.8	pH=11.0
400	1.4	0.10	0.10	0.10	0.40	0.50	1.0
425	1.2	0.04	0.04	0.06	0.12	0.20	0.90
450	1.0	0.04	0.10	0.10	0.11	0.18	0.94
475	0.60	0.04	0.10	0.14	0.20	0.30	0.84
500	0.58	0.08	0.14	0.21	0.30	0.34	0.70
525	0.46	0.10	0.20	0.30	0.40	0.44	0.52
550	0.36	0.04	0.06	0.14	0.24	0.30	0.54
575	0.35	0.02	0.02	0.06	0.10	0.20	0.40
600	0.20	0.01	0.01	0.02	0.14	0.14	0.32

Fig. 17, Curve (1),(2),(3),(4),(5),(6) and (7)

The formation constant was calculated in the similar manner as in case of Cu (ii) and Mn (iii)-D.N.S. complexes.

The values of a_1, a_2, b_1 and b_2 found out from the Job's method curve (Fig. 15) at the O.D. (0.30) were as follows:

$$a_1 = 2.7x2x10^{-3}M \quad b_1 = 7.3x2x10^{-3}M$$

$$a_2 = 4.2x1.25x10^{-3}M, \; b_2 = 5.8x1.25x10^{-3}M$$

Conductometric Studies on Cu (i)- Chromotropic acid (sadium salt) complex.

The Job's method of continuous variation has been extended to other physical properties like conductivity, molar heat content, refractivity etc., and make use of any measurable property of two species in solution, so long as the property has different values for one another. Any complex formed by the interaction of two components must give a value for the same property which is different from the weighted mean of the values for two seperate components.

Purkayastha (loc-cit) applied the molar conductance measurement for the study of Fluoro and Chlora Beryllate. The solutions were prepared according to the method of continuous variation, the conductance of the mixtures were subtracted from the conductances of the two components present in the solution and the difference in conductance

was plotted against the metal concentration present in the mixtures.

Conductometric studies were also carried out to investigate the Cu (i)- D.N.S. complex. Three sets of mixtures were prepared according to the following scheme. The solutions were prepared in air free conductivity water and observations were taken at 30± 1°c.

Set I. Concentration of CuCl = 4.0×10^{-3}M

Concentration of D.N.S. = 4.0×10^{-3}M

Equimolar solutions of CuCl and D.N.S. were mixed in the following ratios.

ratio	1:11, 2:10, 3:9, 4:8, 5:7, 6:6, 7:5, 8:4, 9:3, 10:2, 11:1.
Cu^+	1 cc 2 cc 3 cc 4 cc 5 cc 6 cc 7 cc 8 cc 9 cc 10 cc 11 cc
D.N.S.	11 cc 10 cc 9 cc 8 cc 7 cc 6 cc 5 cc 4 cc 3 cc 2 cc 1 cc

Set II. CuCl (4×10^{-3}m) was mixed with water and the mixtures were prepared in the following ratio.

ratio	1:11, 2:10, 3:9, 4:8, 5:7, 6:6, 7:5, 8:4, 9:3, 10:2, 11:1
Cu^+	1 cc 2 cc 3 cc 4 cc 5 cc 6 cc 7 cc 8 cc 9 cc 10 cc 11 cc
Water	11 cc 10 cc 9 cc 8 cc 7 cc 6 cc 5 cc 4 cc 3 cc 2 cc 1 cc

Set III.

DN.S. ($4x10^{-3}$M) was mixed with water in exactly the same manner as given in set II.

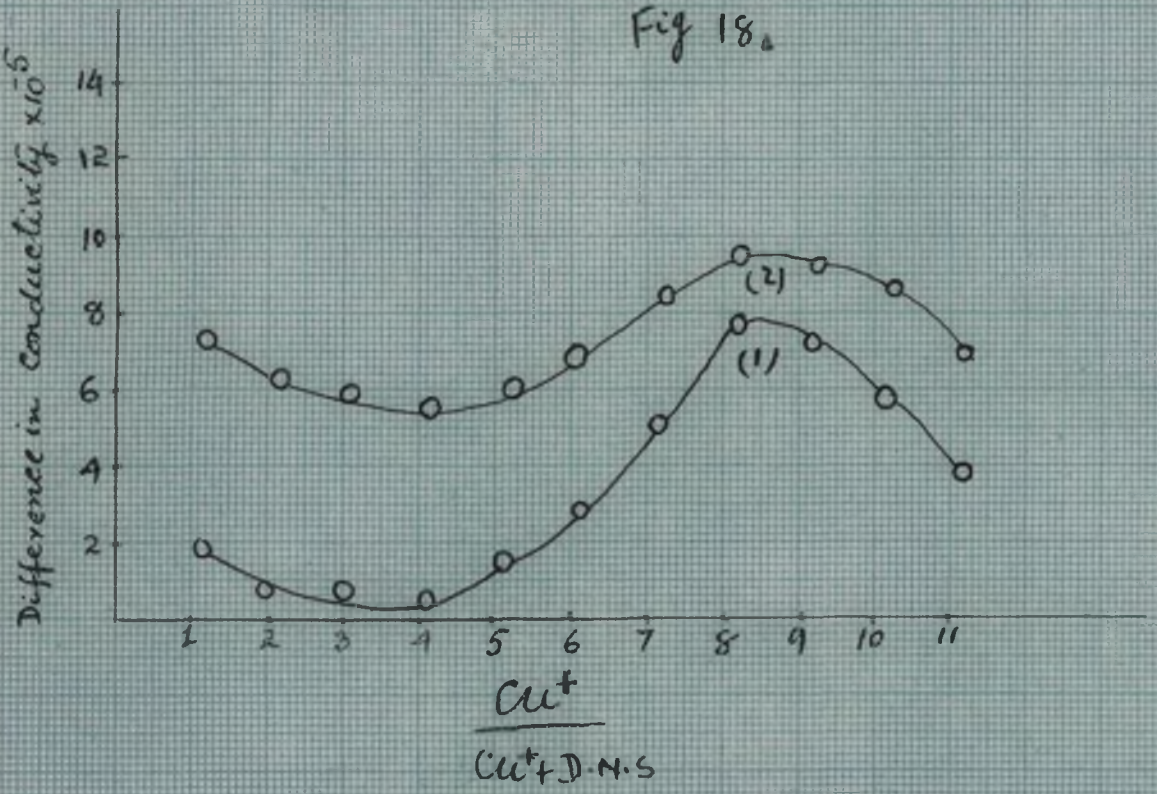
Conductivity measurements were carried out with precision Cambridge conductivity bridge, using a dip type conductivity cell (cell constant = 0.36) recommended for high conductances.

Table 23.

Set I	Set II	Set III		
Conductivity of the complex	Conductivity of Cu^{+} solutions	Conductivity of D.N.S. solutions	Sum of conductivity of Cu^{+} + D.N.S.	Diff. in conductance
$1.94x10^{-2}$	$1.65x10^{-2}$	$4.9x10^{-3}$	$2.14x10^{-2}$	$2x10^{-3}$
$3.35x10^{-2}$	$2.7x10^{-2}$	$7.5x10^{-3}$	$3.45x10^{-2}$	$1x10^{-3}$
$4.2x10^{-2}$	$3.4x10^{-2}$	$8.8x10^{-3}$	$4.28x10^{-2}$	$0.8x10^{-3}$
$5.0x10^{-2}$	$4.4x10^{-2}$	$7.0x10^{-3}$	$5.1x10^{-2}$	$1x10^{-3}$
$6.1x10^{-2}$	$4.8x10^{-2}$	$1.48x10^{-2}$	$6.28x10^{-2}$	$1.8x10^{-3}$
$6.7x10^{-2}$	$5.95x10^{-2}$	$1.50x10^{-2}$	$7.0x10^{-2}$	$3x10^{-3}$
$7.3x10^{-2}$	$6.4x10^{-2}$	$1.40x10^{-2}$	$6.8x10^{-2}$	$5x10^{-3}$
$7.8x10^{-2}$	$6.5x10^{-2}$	$2.08x10^{-2}$	$7.58x10^{-2}$	$7.8x10^{-3}$
$8.5x10^{-2}$	$6.8x10^{-2}$	$2.44x10^{-2}$	$9.24x10^{-2}$	$7.4x10^{-3}$
$8.9x10^{-2}$	$7.8x10^{-2}$	$1.7x10^{-2}$	$9.5x10^{-2}$	$6.0x10^{-3}$
$8.8x10^{-2}$	$8.3x10^{-2}$	$9.0x10^{-3}$	$9.2x10^{-2}$	$4.0x10^{-3}$

Fig. 18, Curve (1)

Fig 18.


Difference in conductivity x10⁻⁵
14
12
10
8
6
4
2
1 2 3 4 5 6 7 8 9 10 11
(2)
(1)
Cu⁺
Cu⁺+D.N.S

Set IV. Concentration of CuCl = 1.66×10^{-3}M

Concentration of D.N.S. = 1.66×10^{-3}M

Equimolar molar solutions of CuCl and D.N.S. were mixed in the same manner as in set I.

Set V. and Set VI. Solutions of CuCl and D.N.S. of concentrations 1.66×10^{-3}M were mixed with water in the sanmer as in set II and III.

Table 24.

Set IV	Set V	Set VI		
Conductivity of the complex.	Conductivity of Cu^{1}	Conuctivity of D.N.S.	Sum of conductivity of Cu^{+} + D.N.S.	Diff. in conductance
3.4×10^{-2}	1.39×10^{-2}	2.75×10^{-2}	4.14×10^{-2}	7.4×10^{-3}
4.2×10^{-2}	2.75×10^{-2}	2.01×10^{-2}	4.76×10^{-2}	5.6×10^{-3}
$4.7c10^{-2}$	1.35×10^{-2}	3.95×10^{-2}	5.30×10^{-2}	6.0×10^{-3}
4.9×10^{-2}	4.15×10^{-2}	1.33×10^{-2}	5.48×10^{-2}	5.8×10^{-3}
5.8×10^{-2}	4.5×10^{-2}	1.94×10^{-2}	6.44×10^{-2}	6.4×10^{-3}
5.1×10^{-2}	5.4×10^{-2}	0.4×10^{-2}	5.8×10^{-2}	7×10^{-3}
6.2×10^{-2}	6.5×10^{-2}	0.54×10^{-2}	7.04×10^{-2}	8.4×10^{-3}
7.2×10^{-2}	6.7×10^{-2}	1.5×10^{-2}	8.2×10^{-2}	1.0×10^{-2}
6.4×10^{-2}	7.2×10^{-2}	0.16×10^{-2}	7.36×10^{-2}	9.6×10^{-3}
7.6×10^{-2}	7.2×10^{-2}	1.3×10^{-2}	8.5×10^{-2}	9×10^{-3}
8.5×10^{-2}	8.4×10^{-2}	8.0×10^{-3}	9.2×10^{-2}	7×10^{-3}

Fig. 18, Curve (2)

The curves were plotted between the diff. in conductance and

$\frac{Cu^{+}}{Cu^{+} + D.N.S.}$

Potentiometric studies on Mn (iii)- D.N.S. complex.

The composition of the Mn (iii)-D.N.S. complex was investigated by carrying potentiometric titrations.

E.M.F. measurements were carried out with pyE precision potentiometer (Type 7568) with lamp and scale arrangement. The indicator electrode was the Mn (iii)-Mn(ii) couple obtained by dipping in a solution of chromotropic acid (sodium salt) containing known amount of Mn (ii). Both direct (D.N.S. in the Cell) and reverse (Mn (iii)SO_4 in the Cell) were performed. The measurements were carried out with different concentration of both the reactants. The reverse titrations, however, did not prove successful and in such cases, no characteristic curves were obtained.

Table 25.

1.0 cc D.N.S. (Set I: $1x10^{-2}$M, Set II: $2x10^{-3}$M and Set III: $5x10^{-3}$M) against $1x10^{-2}$M Mn (iii)SO_4.

Set I		Set II		Set III	
Vol. of Mn(iii)SO_4	Potential vs S.C.E. Volt.	Vol. of Mn(iii)SO_4	Potential vs S.C.E. Volt.	Vol. of Mn(iii)SO_4	Potential vs S.C.E. Volt.
0.5 cc	0.23	0.5 cc	0.135	0.5 cc	0.16
1.0 cc	0.23	1.0 cc	0.125	1.0 cc	0.156
2.0 cc	0.23	1.5 cc	0.115	1.5 cc	0.156
3.0 cc	0.22	2.0 cc	0.080	2.0 cc	0.155
4.0 cc	0.235	2.2 cc	0.055	3.0 cc	0.148
5.0 cc	0.21	2.5 cc	0.50	4.0 cc	0.120
6.0 cc	0.175	3.0 cc	0.50	5.0 cc	0.10
7.0 cc	0.10	3.5 cc	0.50	6.0 cc	0.097
8.0 cc	0.075	-	-	7.0 cc	0.096
10.0 cc	0.04	-	-	-	-
12.0 cc	0.04	-	-	-	-

(Fig. 19, Fig. 20, Fig. 21.)

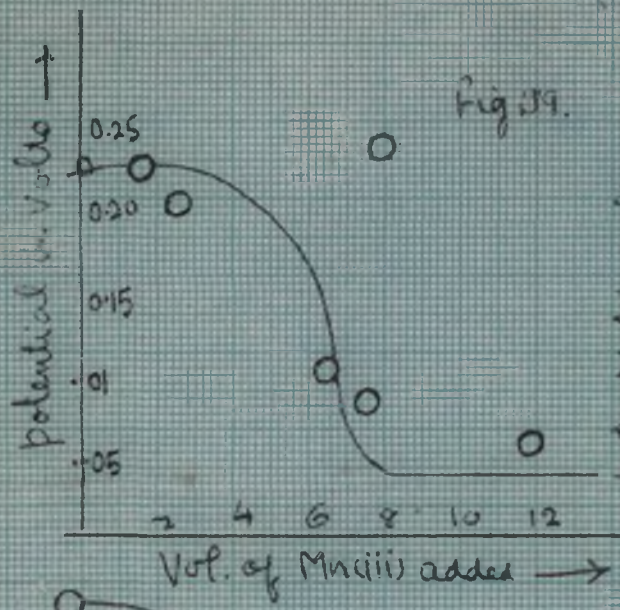


Fig. 19.

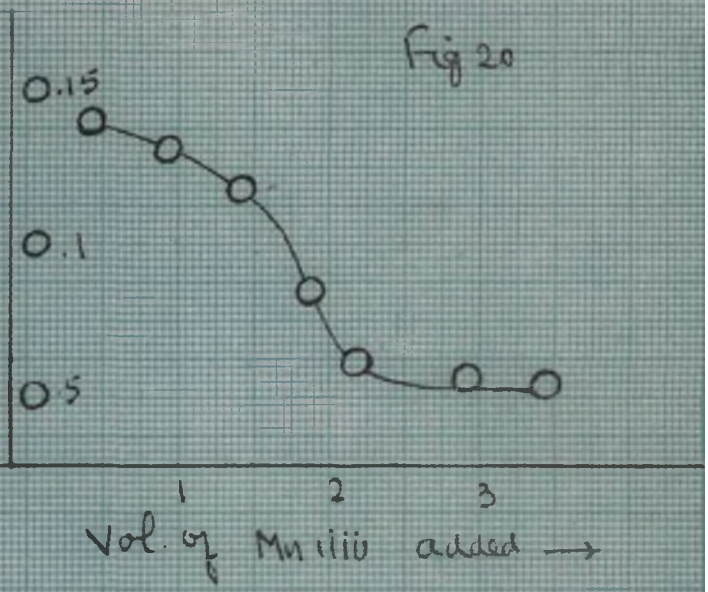


Fig 20

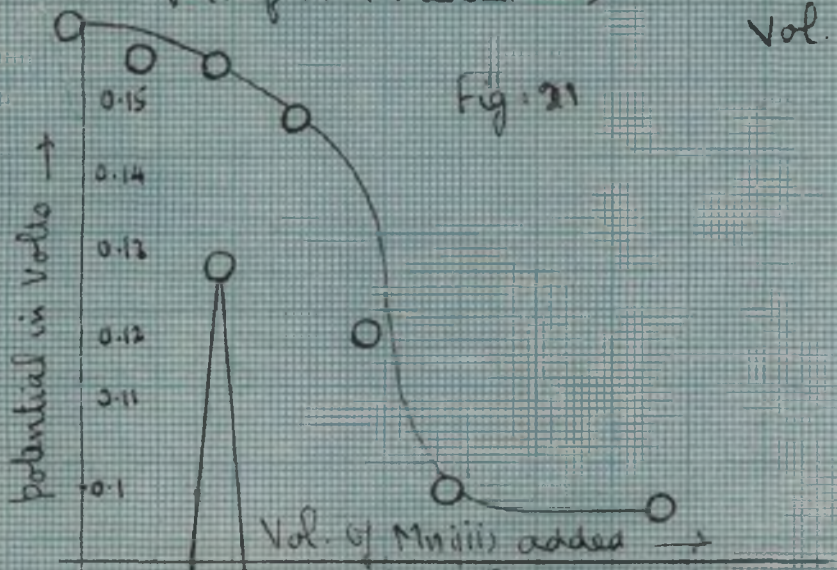


Fig. 21

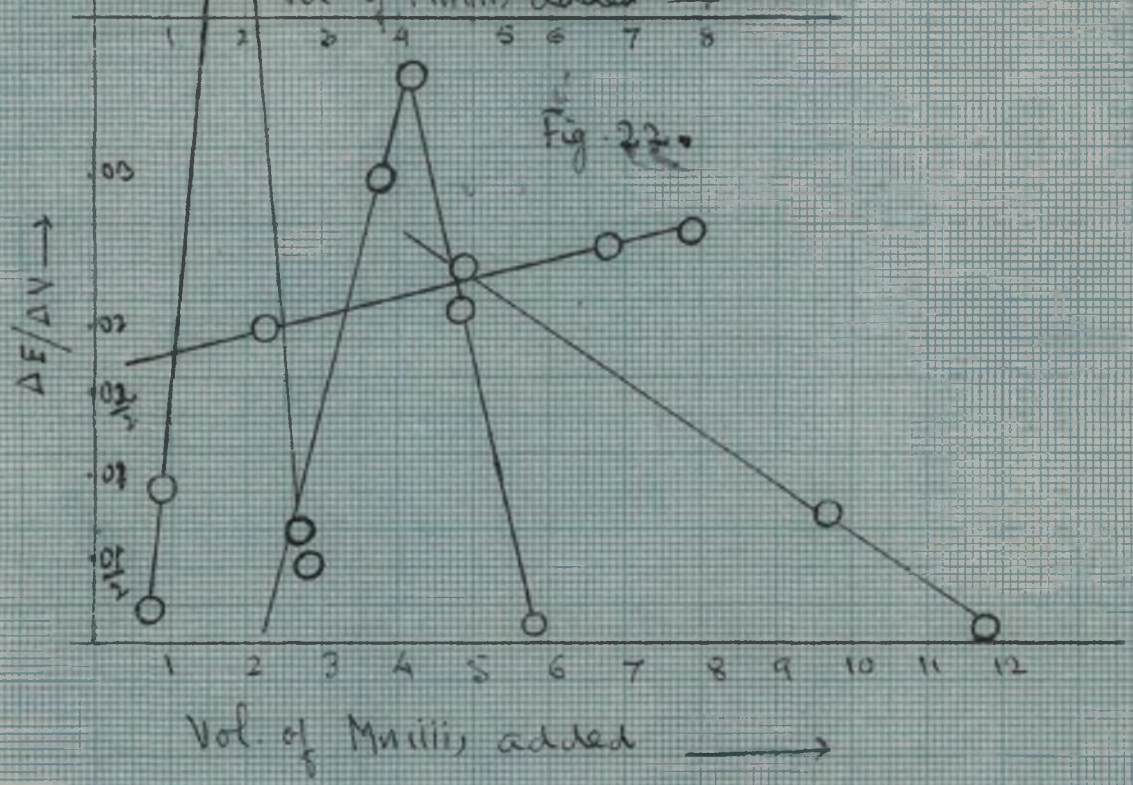


Fig. 22.

Fig. (19) 10 cc $1x10^{-2}$M D.N.S. ≡ $7.2x1x10^{-2}$M Mn(iii)

Fig. (20) 10 cc $2x10^{-3}$M D.N.S. ≡ 2.5 cc$x1x10^{-2}$M Mn(iii)

Fig. (21) 10 cc $5x10^{-3}$M D.N.S. ≡ 4.8 cc $1x10^{-2}$M Mn(iii)

Curves were also plotted between $\frac{\Delta E}{\Delta V}$ and voloume of Mn(iii) added in the Cell, the st. lines of the curves showed sharp points of intersection.

Table 26.

Set I:Conc. of D.N.S.= $5x10^{-3}$M		Set II:Conc.of D.N.S.=$2x10^{-3}$M		Set III:Conc. of D.N.S.= $1x10^{-2}$M	
Vol. of $Mn(iii)SO_4$ added.	$\Delta E/\Delta V$	Vol. of $Mn(iii)SO_4$ added.	$\frac{\Delta E}{\Delta V}$	Vol. of $Mn(iii)SO_4$ added.	$\frac{\Delta E}{\Delta V}$
1 cc	0.002	1 cc	0.01	2.0 cc	0
2 cc	0.0125	1.5 cc	0.01	2.5 cc	0.02
3 cc	0.007	2.0 cc	0.06	5.0 cc	0.024
4 cc	0.03	3.0 cc	0.005	7.0 cc	0.025
5 cc	0.02	4.0 cc	0	8.0 cc	0.026
6 cc	0.01			9.0 cc	0.01
7 cc	0			10.0 cc	0.15

Fig. 22 Curve (1) Fig. 22 Curve (2) Fig. 22 Curve (3)

Curve (1) 10 cc $5x10^{-3}$M D.N.S. ≡ 4.3 cc $1x10^{-2}$M Mn(iii)

Curve (2) 10 cc $2x10^{-3}$M D.N.S. ≡ 1.9 cc $1x10^{-2}$M Mn(iii)

Curve (3) 10 cc $1x10^{-2}$M D.N.S. ≡ 5.2 cc $1x10^{-2}$M Mn(iii)

Polarographic Studies on Cu (ii)-D.N.S. complex:

The polarographic method is unique amongst the electrometric methods to provide precise information regarding the composition and stability of the complexes. However, the most essential condition is that the reduction or oxidation of the metal ion complex should be reversible at the dropping mercury electrode. The study of the metal complexes by the polarographic method based on the fact that the reduction potentials of the metal ions at the dropping electrode are shifted (usually to more negative value) by complex formation, and by this shift as a function of the concentration of the complex forming substance both the formula and the dissociation constant of the complex can be obtained. Lingane[29] has given a comprehensive account on the applicability of polarographic methods to the complex ion formation. According to the author the coordination nop of a complex metal ion. is given by the formula.

$$\frac{E\ 1/_2}{\log Cxf_x} = -p\ \frac{.0591}{n}$$

where C_x is the concentration of complexing agent and f_x is activity Coefficent which may be given the value of unity with sufficient accuracy, $E1/_2$ is the shift in half wave potential and n is the no. of electron transfer involve in the electrode reaction.

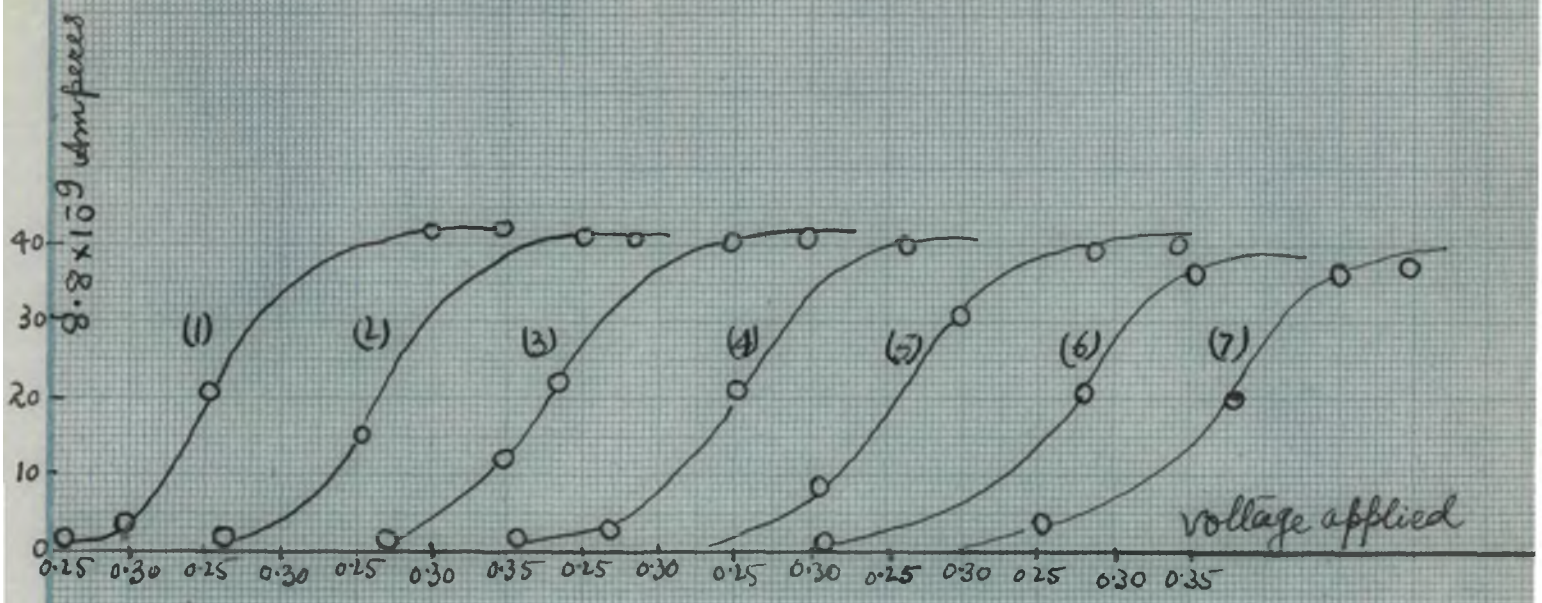
Polarographic studies on Cu (ii)-D.N.S. complex were carried in order to determine the composition of complex .

Fischer/Elecdropode with multiflex galvavemeter (MGF-2) in the external coriuit was used for polarographic measurements. All the experiments were carried out at 30± 0.1°C using a water thermoertatic bath (Townsen and Mercer Ltd.). The inert atmosphere in the cell was maintained by bubbling nitrogen after passing it through alkaline pyragallol and chromus chloride solution.

Cupric chloride (Anala R) of concentration $1x10^{-2}$M and D.N.S. of the concentration $2x10^{-2}$M were prepared, KCl (Anala R) of concentration (1M) and methyl red (0.01%) were respectively used as supporting eleclrolyte and maxima suppressor. The buffer solutions used (Walpole acetate buffer for pH 6 to 7 and phosphate buffers for the pH beyond 7) were prepared from A.R. products.

Polarography of about forty mixtures were carried out at different concentrations and pH's. The observations are summerised in the following tables:

Fig 23.



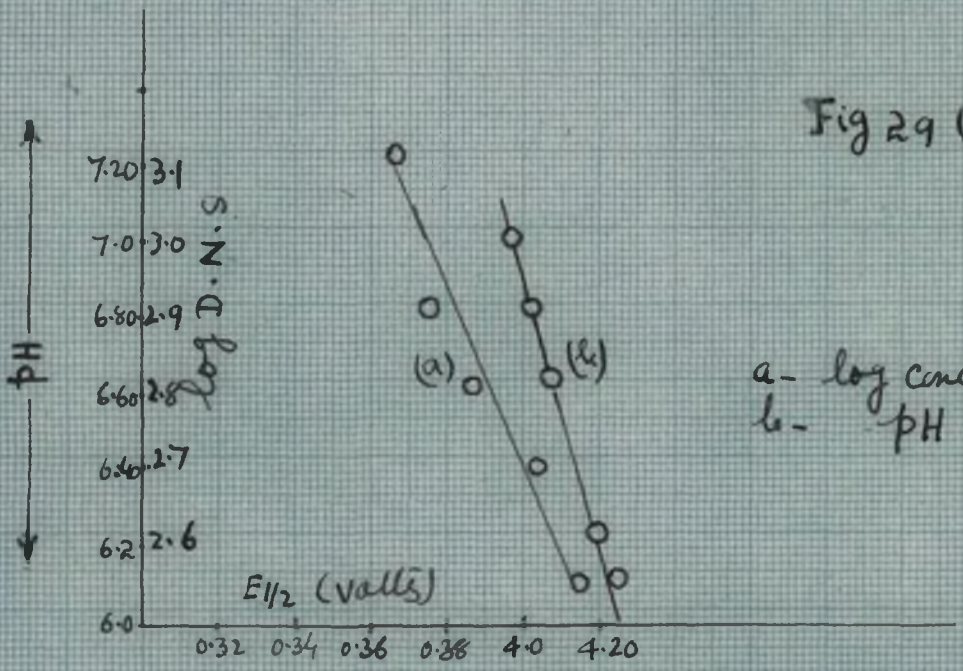


Fig 29 (facing page 81)

a- log conc D.N.S
b- pH

Table 27.

Polarograms of $1x10^{-4}$ M/ $CuCl_2$ in $8x10^{-1}$ M/KCl in presence of different concentrations of D.N.S. at pH= 6.5

Potential applied curve No: (in Volts).	CURRENT ($8.8x10^{-9}$) ampere						
	1 $0.8x10^{-2}$	2 $1.2x10^{-2}$	3 $1.6x10^{-2}$	4 $2.0x10^{-2}$	5 $2.4x10^{-2}$	6 $2.8x10^{-2}$	7 $3.2x10^{-2}$
0	-15.0	-12.0	-12.0	-12.0	-11.5	-12.0	-12.0
0.20	0	0	0	0	0	0	0
0.25	0	0	0	0	0	0	0
0.30	3.0	4.0	3.5	1.0	3.0	2.0	2.5
0.35	8.0	14.0	10.0	10.0	7.0	3.0	5.0
0.40	21.0	30.0	25.0	19.0	18.0	10.0	8.0
0.45	30.0	38.0	35.0	33.0	30.0	17.5	20.0
0.50	36.0	40.0	40.0	39.0	37.0	35.0	30.0
0.55	38.0	40.0	40.0	40.0	40.0	38.0	36.0
0.60	40.0	41.5	41.5	40.0	40.0	38.0	37.0
0.70	40.0	41.5	42.0	40.0	40.0	38.0	37.0
0.80	40.0	41.5	42.0	40.0	40.0	38.0	37.0

Fig. 23.

Fig. 24

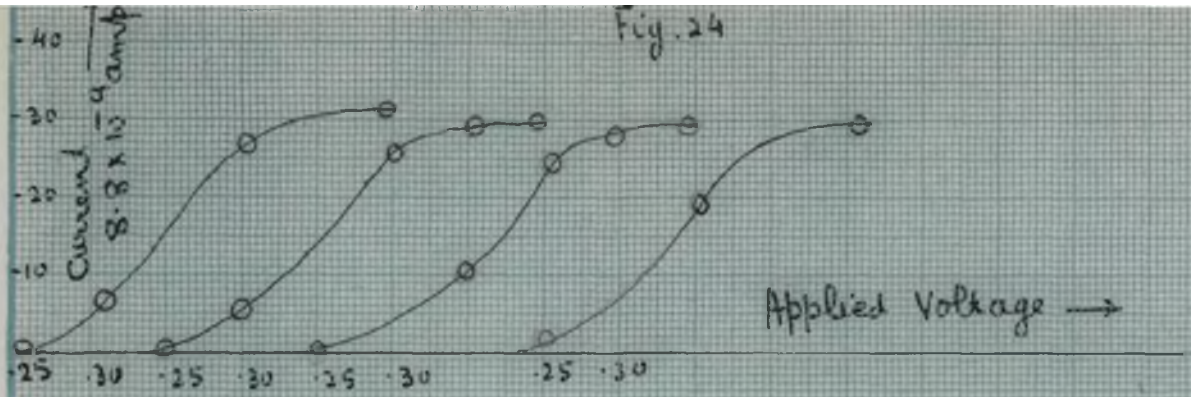


Fig. 28

(1) pH = 8·3

(2) pH = 9·9

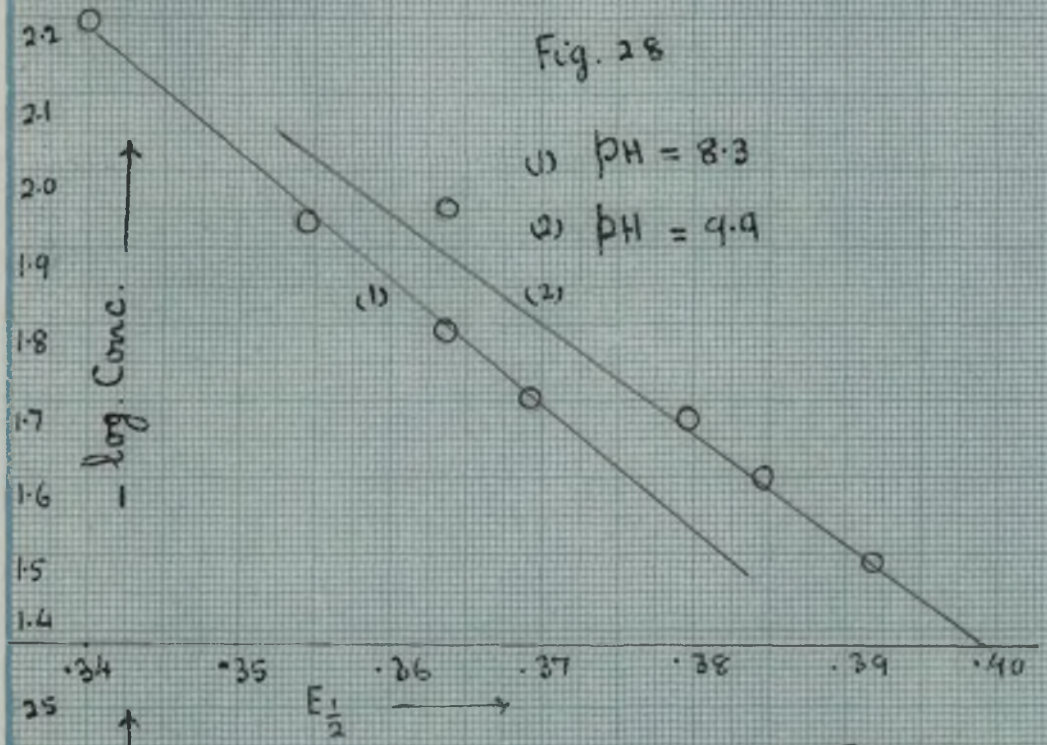


Fig. 25

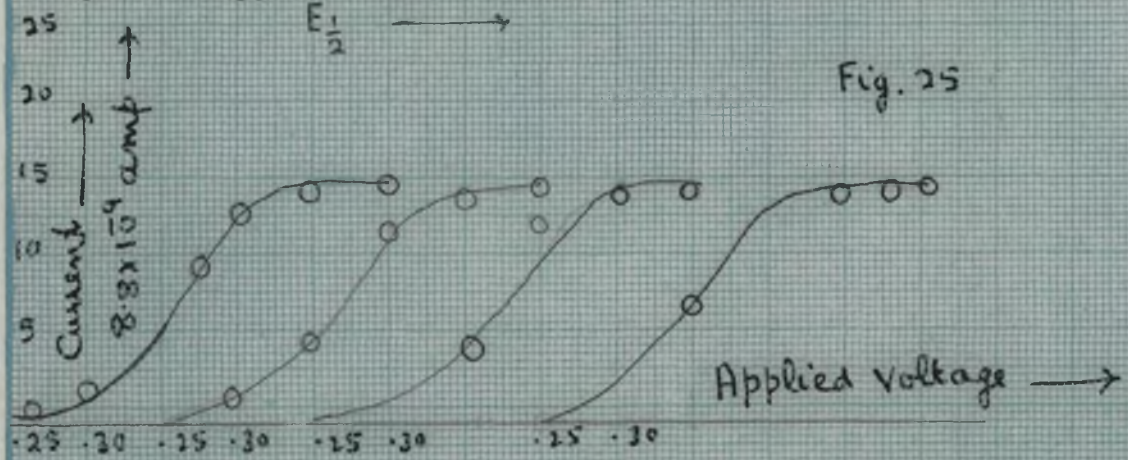


Fig. 26

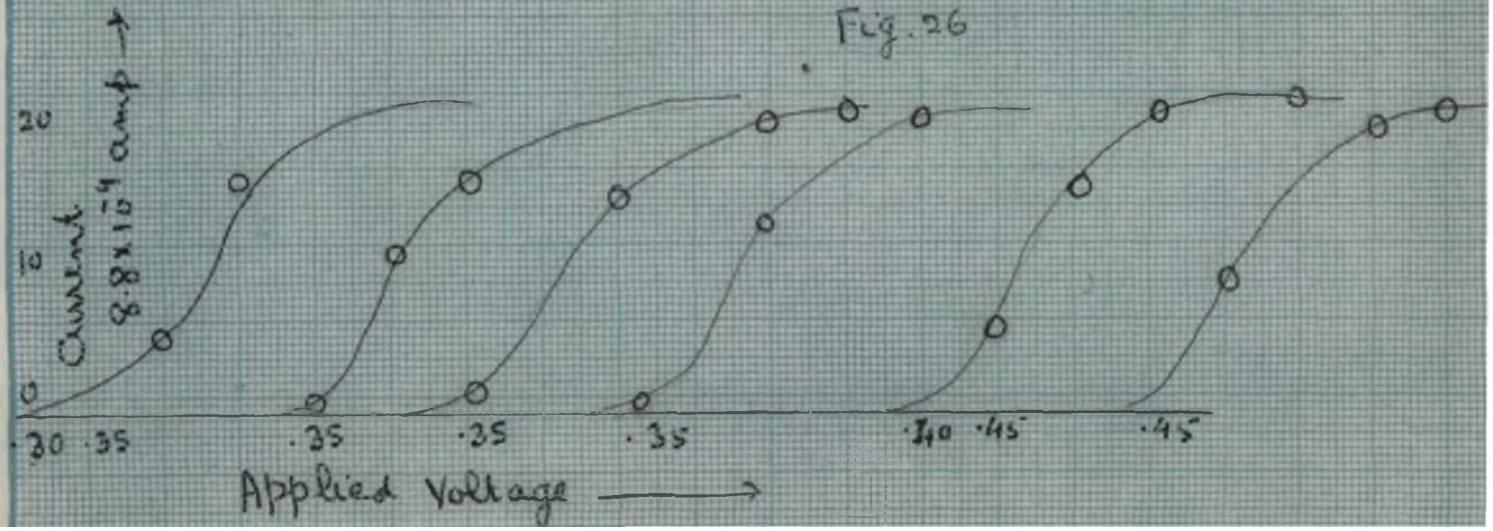


Table 28.

Set I. Polarograms $1x10^{-4}$M $CuCl_2$ in $8x10^{-1}$M KCl in presence of different concentrations of D.N.S. at pH= 8.3.

Set II. Polarograms of $1x10^{-4}$M $CuCl_2$ in $8x10^{-1}$M KCl in presence of different concentrations of D.N.S. at pH= 9.9.

Set I	pH=8.3				Set II	pH=9.9		
Potential applied.	Current ($8.8x10^{-9}$) ampere.				Current ($8.8x10^{-9}$) ampere.			
	1 $8x10^{-3}$	2 $1.6x10^{-2}$	3 $4x10^{-2}$	4 $3.2x10^{-2}$	1 $8x10^{-3}$	2 $1.6x10^{-2}$	3 $2.4x10^{-2}$	4 $3.2x10^{-2}$
0	-11.5	-12.0	-12.0	-12.0	-15.5	-14.0	-16.0	-22.0
0.25	0	0	0	2.0	0	0	0	- 1
0.30	6.0	5.0	4.0	7.0	1.5	1.5	0.5	0
0.35	15.0	14.0	10.0	20.0	-5	5.0	5.0	0.5
0.40	26.0	25.0	24.0	27.0	10	12.0	10.0	7.5
0.45	30.0	28.0	28.0	30.0	13.5	14.5	14.5	14.5
0.50	30.0	29.0	29.0	31.0	15	15.0	15.0	15.0
0.55	30.0	30.0	30.0	31.0	15.5	15.0	15.0	15.5
0.60	30.0	30.0	30.0	31.0	15.5	15.0	15.0	15.5
0.70	30.0	30.0	30.0	31.0	15.5	15.0	15.0	15.5
0.80	30.0	30.0	30.0	31.0	15.5	15.0	15.0	15.5
1.0	30.0	30.0	30.0	31.0	15.5	15.0	15.0	15.5

Fig. 24.

Fig. 25.

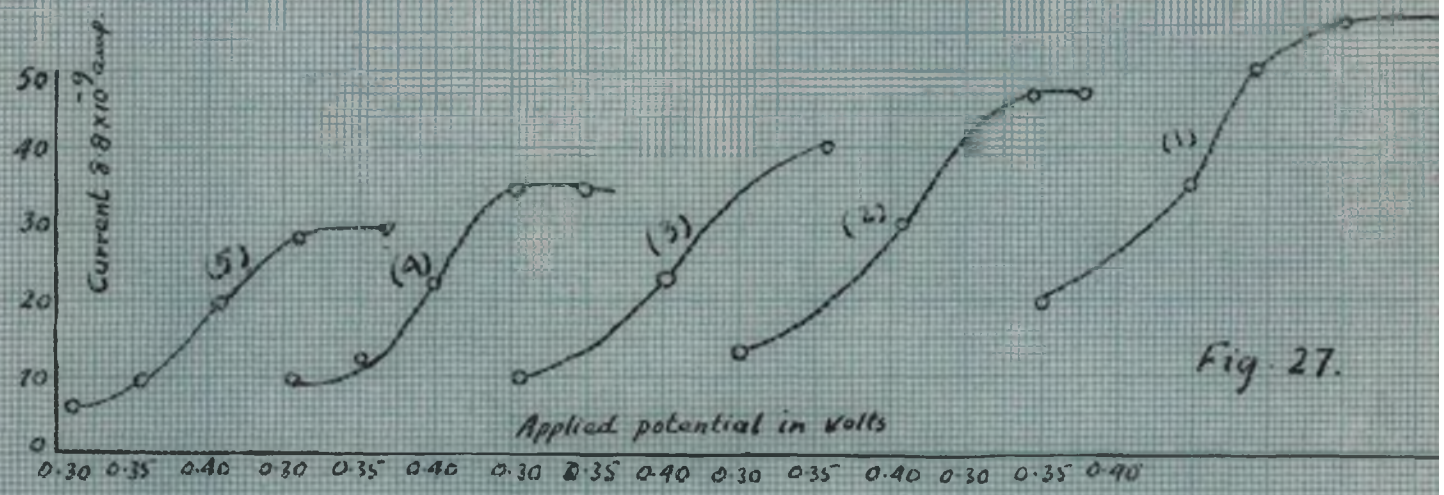

Current $\times 8 \times 10^{-9}$ amp.
50
40
30
20
10
0
(5)
(4)
(3)
(2)
(1)
Applied potential in volts
0·30 0·35 0·40 0·30 0·35 0·40 0·30 0·35 0·40 0·30 0·35 0·40 0·30 0·35 0·40

Fig. 27.

Table 29.

Polarogram of $1x10^{-4}$ $CuCl_2$ in $8x10^{-1}$M KCl in presence of different concentrations of D.N.S. at pH= 11.0

Potential applied (in Volts)	Current($.88x10^{-9}$ ampere) 1 $8x10^{-3}$	2 $1.2x10^{-2}$	3 $1.6x10^{-2}$	4 $2.0x10^{-2}$	5 $2.4x10^{-2}$	6 $2.8x10^{-2}$	7 $3.2x1$
0	-11.5	-11.5	-11.5	-11.0	-11.0	-12	-12
0.3	0	-2.25	- 4.5	4.0	0	0	0
0.35	2.0	0,5	0	0	0	0	0
0.40	5.0	10.0	3.5	0.5	1.0	0	0
0.45	14.0	15.0	12.5	6.5	6.5	1.0	1.0
0.50	17.0	18.0	16.5	15.0	15.0	11.0	3.5
0.55	20.0	19.0	19.0	19.5	20.0	15.0	11.0
0.60	20.0	20.0	20.0	19.5	20.5	19.0	15.0
0.65	20.0	20.0	20.0	19.5	20.5	19.5	18.0
0.70	20.0	20.0	20.0	19.5	20.5	19.5	19.0

Fig. 26.

Table 30.

Concentration of $CuCl_2$ = $1x10^{-4}$M

Concentration of D.N.S.= $1.6x10^{-2}$M

Potential applied (in Volts)	Current($.8x10^{-9}$ ampere) 1 pH=6.1	2 6.2	3 6.6	4 6.8	5 7.0
0	-1.25	-3.0	-3.75	-5.0	-5.0
0.1	5.75	3.75	2.225	1.75	0.75
0.2	11.5	8.5	5.75	6.5	4.0
0.3	18.0	13.5	9.5	10.0	6.75
0.35	25.0	18.0	26.0	10.5	9.0
0.40	30.0	29.0	38.0	21.0	18.0
0.45	50.0	50.0	40.0	34.0	28.0
0.50	56.0	50.5	40.5	35.0	30.0
0.55	56.0	50.5	40.5	35.0	30.0
0.60	56.0	50.5	40.5	35.0	30.0

Fig. 27.

D I S C U S S I O N

Composition of Cu(i)-Chromotropic acid (sodium salt) Complex:

Preliminary experiments carried out to study the reaction between cuprous chloride and chromotropic acid (sodium salt) showed that the reaction was a slow one and took about 6 to 12 hours for completion depending upon the concentration of the reactants. Thus with dilute solutions ($1.0x10^{-3}M$ to $2.5x10^{-3}M$) it took 12 hours for reach completion where as with relatively concentrated solutions ($1x10^{-2}M$ to $2.5x10^{-3}M$) the upper limit was approximately six hours. The complex was pink in colour.

The spectrophotometric methods employed to study the Cu (i)- D.N.S. reaction gave the following information regarding the composition of the complex.

(i) Vosburgh and Cooper's method was employed to determine the number of complexes formed by the interaction of CuCl and D.N.S. Equimolar molar solutions ($2x10^{-3}M$) of the reactants were mixed in the ratio of Cu^{+}: D.N.S. as 2:8, 3:7, 4:6, 5:5 etc. and kept for more than six hours and their O.D. were measured in the wave length range of 400 mu to 600 mu. All the mixtures showed that the absorption maxima existed at 430 mu thereby showing the existence of only one complex. (Table No. 1 Fig. No. 1).

(ii) Job's method was followed for determining the composition of Cu(i)-D.N.S. complex. Solutions of CuCl and D.N.S. of concentrations 2.5×10^{-3}M, 2×10^{-3}M, 1.25×10^{-3}M and 1.0×10^{-3}M were prepared according to the method of continuous variation, and optical densities were measured at 430 mu after 6 to 12 hours of mixing (in order to ensure that the reaction had completed). The CuCl and D.N.S. at these concentrations had a negligible small absorption. The O.D. density curves plotted against the ratio $\frac{Cu^{+}}{Cu^{+}+D.N.S.}$ gave a combining ratio of 2:1 for Cu^{+} and D.N.S. (Table No. 2 and 3, Fig. No.2).

(iii) The results were confirmed by slope ratio method. Two sets of experiments were performed. In the first set the concentration of D.N.S. was kept constant and that of cuprous chloride was varied, in the other set the mixing was done in the reverse order. Similarly two more sets of experiments were carried out at different concentrations (Table No. 4 and 5 and Fig. No. 3). The slope was determined over the St. line portion of the curve and again the combining ratio 1.7:1 or Cu^{+} and D.N.S. was obtained.

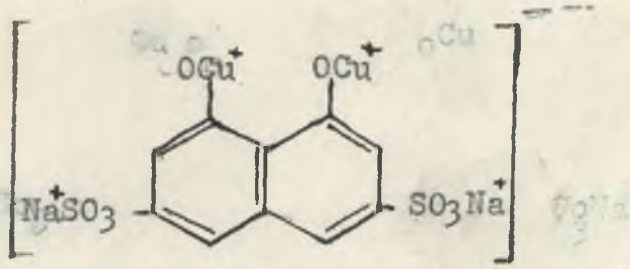
(iv) A combining ratio of 1.9:1 for Cu^{+} and D.N.S. was furthur evaluated by applying modified slope ratio method. The point of intersection of two curves (Fig. 4) corresponds to the required ratio.

(v) The influence of pH on the absorption of the complex was investigated by measuring the absorbances of the mixtures of equimolar solutions ($1x10^{-3}$M) of CuCl and D.N.S. in the wave length range 400 to 600 mu . The absorbance curves showed that maxima at λ_{max} = 430 mμ was only realised in the pH range 5 to 7 (Table No. 6 Fig. No. 5). This shows that the complex is stable in this pH range.

The value of formation constant K was(calculated by using the equations given on page 39) come out to be $2.1x10^{4}$ at the O.D. 1.1 and the free energy of formation calculated from the relation $-\Delta F^{o} = RT\ln K$ worked out to be -2.58 KCals at 30°C (Fig. No.2).

Electrical conductance measurements were made with mixtures prepared according to Job's method (Table No. 23 and 24). The difference in sp conductivity (Sum of the conductivities of the reactants minus the observed conductivity of the complex) was plotted against the composition of the mixtures (Fig. No. 18). From the curves it would be concluded that the components (Cu^{+} and D.N.S.) interacted in the ratio of 2:1 .

From the information arrived at by the spectrophotometric and conductometric measurements, the complex may be formulated

as 

In case of chromotropic acid, the general tendency of hydroxyl group is to coordinate with metal ions and to form close ring structures viz., complexes of Ti(iv), Fe(iii) etc. However, in case of Cu^{+} ions only one possibility exists that is the removal of two H^{+} ions by two Cu^{+} ions giving thereby an open structure. Though, very few complexes are reported in which the metal and complexing agent ratio exceeds to one but they are not completely extinct. For example the copper complexes of 2[1] hydroxy-5[1] sulphobenzene azo-β - naphthol showed[30] on analysis the copper dye ratio of 2:1 and the same ratio was found for the complexes of metalphthal-ems[31] with Ba, Sr, Ca etc. Also, the metal dye complexes known as dye lake are classified in two catagories (i) coordination complexes and (ii) metal-dye salts.[32] The Cu(i) complex seems to belong the latter group of compounds.

Absorption studies carried out with different ratios of Cu^{+} and D.N.S. at v-arying concentrations of the reactants lead to the conclusion that the reaction between Cu^{+} and D.N.S may be utilized for the estimation of Cu^{+} ions coloremetrically. The results with considerable accuracy may be obtained by keeping the solutions for 6 to 12 hours to complete the reaction and in absence of such interfering metal ions as

Fe (iii), Cu (ii), Ti (iv) etc.

Composition of Cu (ii)-Chromotropic Acid (sodium salt) Complex:

Cupric chloride and the sodium salt of chromotropic acid on interaction gave a soluble complex red in colour. The reaction was quite slow and took 2 to 3 hours for completion in the concentration range 2.5×10^{-3}M to 5×10^{-4}M. With more dilute solutions the time for completion increased considerably and sometimes it took 12 hours for red colour to develop. The composition of the complex was studied spectrophotometrically and polarographically. On the basis of spectrophotometric studies, the following information was obtained regarding the composition of the complex.

(i) Vosburgh and Cooper's method was applied to determine the number of complexes formed. (Reactants each of concentration 1×10^{-3}M were mixed in the ratio Cu^{++}: D.N.S. as 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 respectively and their absorbances were measured in the wave length range of 400 to 650 mu (Table No. 7, Fig. No. 6). All the solutions gave a maxima at 525 mu , showing thereby the formation of only one complex.

(ii) Results of Job's method (carried out at the wave length 525 mu) for the 3 sets of concentrations (1.66×10^{-3}M, 1.25×10^{-3}M and 1.0×10^{-3}M) gave a combining ratio of 1:1 for Cu^{++}: D.N.S. (Table No. 8, Fig. No. 7).

(iii) The results were furthur confirmed by the slope ratio method. In the latter case concentrations of D.N.S. ($1x10^{-3}M$) was kept constant and $CuCl_2$ of concentration $2.5x10^{-3}M$ was added in varying amount in one set, while in the other the concentration of D.N.S. ($2.5x10^{-3}M$) was varied, keeping the concentration of $CuCl_2$ ($1x10^{-3}M$) constand. Similarly, two more sets of solutions were prepared and O.D. was measured at 525 mu . The slopes over the st. line portion of the curves gave a combining ratio of 1:1 (Fig. No.8, Table No.9 and 10).

The formation constant was calculated with the help of the expressions given on page 49. Taking two concentrations of Cu^{++} ($3.1x1.66x10^{-3}M$ and $3.6x1.25x10^{-3}M$) and D.N.S. ($6.9x1.66x10^{-3}M$ and $6.4x1.25x10^{-3}M$) at the same O.D. (0.70), the value of x from the equations came out to be $5.11x10^{-4}M$ and the value of K was found to be $2.28x10^{5}$. The free energy of formation $-\Delta F^{o}$ was estimated to be - 3.767 K Cals.

In order to study the influence of pH on the absorbance maxima, solutions of the reagents of concentration $1x10^{-2}M$ were prepared in the ratio 1:1 and then diluted with buffers to 10 cc. The absorbances measured in the wave length range of 400 mu to 650 mu showed the existence of only one maxima at 525 mu in the pH range 6.0 to 11.0, thereby showing that the complex was stable in this pH range (Table No.10, Fig.No.9

The composition of Cu^{ii}- D.N.S. complex was furthur investigated polarographically. The polarograms (Table No. 27, 29 and 30, Fig. No. 23, 24, 25, 26 and 27) showed that the reduction of Cu^{ii}- D.N.S. complex was reversible at the dropping mercury electrode with one electron transfer as the values of $E\ 3/4 - E\ 1/4$ (Tome's method)[33] were found to be between 0.055 and 0.065.

Polarography of some forty mixtures was carried out. The results are summerised in the following table.

Table No. 30.

Conc. of $CuCl_2 = 1x10^{-4}M$ Conc. of $CuCl_2 = 1x10^{-4}$ M

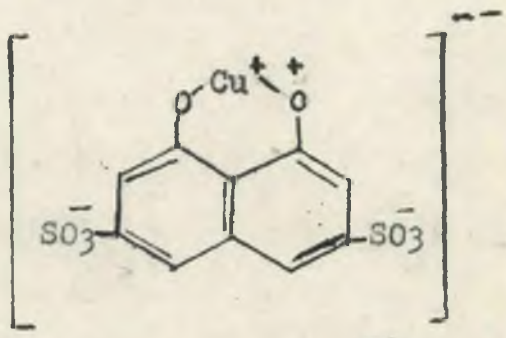
Conc.of D.N.S.$= 1.6x10^{-2}$ M

Conc. of D.N.S.$x10^{-2}$M	-Log Conc. of D.N.S.	$E1/_2$ (pH= 9.9)	$E1/_2$ (pH= 8.3)	$E1/_2$ (pH= 11.0)	$E1/_2$ (pH= 6.5)	pH	$E1/_2$
0.80	2.2	0.365	0.340	0.43	0.365	6.1	0.425
1.2	1.92	-	-	0.45	0.375	6.2	0.420
1.6	1.80	0.380	0.365	0.465	0.385	6.6	0.410
2.0	1.70	-	-	0.470	0.405	-	-
2.4	1.61	0.385	0.370	0.480	0.415	6.8	0.40
2.8	1.55	-	-	0.52	0.420	7.0	0.395
3.2	1.50	0.390	0.385	0.56	0.430	-	-

(Vide infra Fig. 23,24,25 and 26) (Vide infra Fig. 27)

Frome the foregoing observations tabulated above, it is evident that $E1/_2$ values were found to depend both upon the concentration of D.N.S. and the pH of the medium $E1/_2$ values[34] were plotted against-log conc. of D.N.S. at pH= 6.5, 8.3 and 9.9 to determine the number of D.N.S. molecules associated with one atom of copper (Fig. 28, 29). From the slope of the st. line the value came out to be 0.065, showing that one atom coordinates with one molecule of D.N.S. Also on plotting $E1/_2$ versus pH[35], a st. line is obtained having the slope of 0.03, showing that two hydroxyl groups coordinate with one atom of copper (Fig.No.29

On the basis of spectro-photometric and polarographic studies, the structure of the complex may be formulated as



Composition of Mn (iii)- Chromotropic Acid (sodium salt) complex

Manganic sulphate formed a yellow coloured complex with sodium salt of chromotropic acid. The reaction took place in highly acidic solution and has not yet been studied. Spectrophotometric and potentiometric studies were carried to investigate the composition of the complex.

Vosburgh and Cooper's method was employed to determine the no. of complexes formed. Absorbances of the mixtures of equimolar solutions ($1x10^{-2}M$) of D.N.S. and Mn (iii) SO_4 in the ratio of 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 respectively were measured in the wave length range of 350-650 mu (Table No. 11. Fig. No. 10). Absorption curves showed the presence of a single absorption peak at 430 mu, thereby indicating the formation of only one complex. The absorption spectra of Mn (iii)SO_4 was also studied, absorption curves showed that λ_{max} of Mn (iii)SO_4 was found to be at 515 mu (Table No. 12, Fig. 11).

The composition of the complex was determined by employing Job's method of continuous variation and slope ratio method.

Equimolar solutions of Mn (iii)SO_4 and D.N.S. ($2.5x10^{-3}M$, $1.66x10^{-3}M$, $1.25x10^{-3}M$ and $1.0x10^{-3}M$) were mixed according to the method of continuous variation and their absorbances were measured at 430 mu (Fig. No. 12). The absorbances of Mn (iii)SO_4 and D.N.S. were found to be negligible at this concentration range. It was found that the complex was formed in the molar ratio Mn (iii): D.N.S. as 1:1.

The composition of the complex was further investigated by the slope ratio method. Two series of solutions were prepared by varying the concentration of one of the reagents in presence of a constant excess of the other and their absorbances were measured at 430 mu (Table No. 15, 16 and Fig. No. 15). From the slopes here too, the ratio of Mn(iii): D.N.S. was found to be 1:1.

It was observed that in solutions of pH $\gtrsim$1, the colour of the complex was completely destroyed, hence the extinction measurements could only be done in presence of dil H_2SO_4. The effect of pH on the colour intensity and the formation of complex, therefore, remained uninvestigated.

The value of formation constant of the complex was determined by the method described on page 49. For two concentrations of Mn^{+++} ($6.2x1.25x10^{-3}$M and $6.6x10x10^{-3}$M) and D.N.S. ($3.8x1.25x10^{-3}$M and $3.4x10x10^{-3}$M) having the same optical density 0.20 the value of K came out to be $1.8 \times 10^{+5}$ and that of free energy ($-\Delta F^{o}$) was found to be -3.11 K Cals at 30°C.

The composition of Mn(ii) + D.N.S. complex was also investigated by carrying out potentiometric titrations. The electrodes used were: bright pt indicator electrode dipped in a solution of Chromotropic acid (containing known amount of Mn(iii) SO_4 thus forming a $Mn^{+++} \rightleftharpoons Mn^{++} - e$ couple) and calomel electrode working as reference electrode. D.N.S. solutions of varying concentrations ($1x10^{-2}$M, $5x10^{-3}$M and $2x10^{-3}$M) ware titrated with manganic sulphate ($1x10^{-2}$M) solution.

The curves showed sharp breaks. The results are summerised as follows:

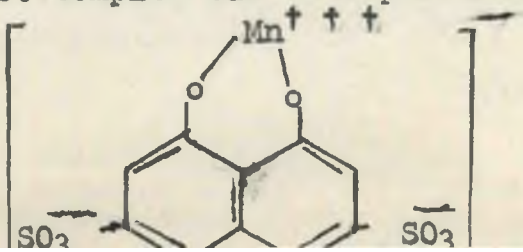
	ratio at the point of inflexion.
a) 10 cc of $1x10^{-2}$M D.N.S.=7.2 cc $1x10^{-2}$M Mn(iii) (Fig. No.19, Table No. 25).	1:1.3
b) 10 cc of $5x10^{-3}$M D.N.S.=4.8 cc $1x10^{-2}$M Mn(iii) (Fig. No. 20, Table No. 25).	1:1.04
c) 10 cc of $2x10^{-3}$M D.N.S.=2.5 cc $1x10^{-2}$M Mn(iii) (Fig. No. 21, Table No. 25).	1:1.0

Also the $\frac{\Delta E}{\Delta V}$ verses voloume of Mn (iii) added curves gave sharp points of intersection, the results are as follows:

	ratio at the point of intersection.
10 cc $5x10^{-3}$M D.N.S.=4.3 cc $1x10^{-2}$M Mn (iii)	1: 1.14 (1)
10 cc $2x10^{-3}$M D.N.S.=1.9 cc $1x10^{-2}$M Mn (iii)	1: 1.05 (2)
10 cc $1x10^{-2}$M D.N.S.=5.2 cc $1x10^{-2}$M Mn (iii)	1: 1.7 (3)

The potentiometric method gave information for 1:1 complex, as indicated from the above results. The reverse titrations, however, did not prove successfull and there were no significent breaks in the curves.

On the basis of above information the structure of Mn (iii)- D.N.S. complex can be represented as



The indication of complex ion formation between Mn(iii) and D.N.S. in the highly acidic medium combined with the fact that a fairly stable colour is developed can be advantageously employed for the colorimetric estimation of Mn(iii) in small amounts.

Composition of V(iv) - Chromotropic Acid (Sodium Salt) Complex.

The formation of a brown coloured product by the interaction of vanadium salts with chromotropic acid was mentioned by some authors but details about its behaviour and composition are lacking. In our case, vanadyl sulphate was found to form a red coloured soluble complex with chromotropic acid and its composition was determined by applying spectrophotometric methods.

Preliminary experiments showed that the reaction between vanadyl sulphate and D.N.S. was a slow one, solutions in the concentration range (2.5×10^{-3}M to 1×10^{-3}M) took about six hours for completion, while solutions in the concentration range of 1×10^{-3}M to 2×10^{-4}M took more than twelve hours (the completion of the reaction indicated by the development of coloured in the solutions).

Equimolar solutions (2.5×10^{-3}M) of vanadyl sulphate and D.N.S. were mixed in the ratio of 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 and were kept for about six hours to ensure complete

reaction, their optical densities were measured at different wave lengths (400 mu to 600 mu). The maximum absorption for all mixtures was found at 525 mu, indicating the formation of only one complex (Fig. No. 14; Table 17).

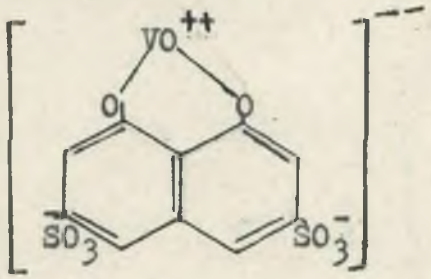
For the method of continuous variation foursets of mixtures of equimilar concentration (2.5×10^{-3}M, 2.0×10^{-3}M, 1.66×10^{-3}M and 1.25×10^{-3}M) were prepared and O.D. was determined at 525 mu. The absorption of vanadyl sulphate and chromotropic acid was negligible at this concentration. The O.D. was plotted against the ratio VO^{++}/ VO^{++} + D.N.S. (Table No. 18 and 19, Fig. No. 15). The combining ratio of 1:1 was obtained by the curves.

In the case of slope ratio method, the concentration of D.N.S. (2×10^{-3}M) was kept constant and the concentration of vanadyl sulphate varied (2×10^{-4}M to 2.5×10^{-3}M) in one set, while in the other the concentration of D.N.S. (2×10^{-4}M to 2.5×10^{-3}M) was varied, keeping the concentration of VO^{++} (2×10^{-3}M) constant. Similarly two more sets of solutions were prepared and their absorbances were noted at 525 mu. The slopes over the straight line portion of the curve gave a ratio of 1:1 for the complex. (Table No. 20 and 21, Fig. 16).

The influence of pH on the formation of the complex was investigated by using equimolar solutions (1×10^{-2}M) of the reactants in the ratio of 1:1 and then diluting then ten

times by the buffers prepared from A.R. products. The absorbances of these solutions were measured (Table 22, Fig. 18). Maxima at λ_{max} = 525 mu was only realised in the pH range 6.7 x 11.0.

On the basis of spectrophotometric measurements, the composition of the complex may therefore be depicted as VO^{++} (D.N.S.) and its structure as



The value of formation constant was calculated with the help of the expressions given on page 49. For two concentrations of vanadyl sulphate (2.7 x 1 x 10^{-3}M 4.2 x 1.25 x 10^{-3}M) and D.N.S. (7.3 x 2 x 10^{-3}M, 5.8x1.25 x 10^{-3}M at the O.D. (0.30), the value of x was found to be 4 x 10^{-4}M and from this the value of formation constant was found to be 3.99 x 10^{+3} and that of free energy of the reaction came out to be $-\Delta F$ = 2.67 K Cals at 20°c.

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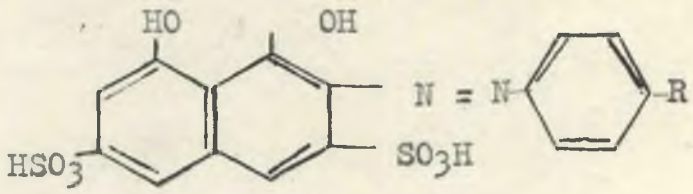
C H A P T E R II.

Cu(ii)-Chromotrope 2B complex

Cu(ii)-CHROMOTROPE 2B COMPLEX

In recent years, a number of communications have been published on the analytical uses of substituted chromotropic acid and azochromotrope compounds. The latter compounds are characterised by having an esterfiable phenolic hydroxy group with respect to N-atom of the azo group, and it is through this group that chelation is said to take place. Datta[1] discussed the analytical applications of azo chromotropic acids and Banerjee[2] used some of these reagent for the spectrophotometric determination of thorium and zirconium. Tolmachev and Lemaskana[3] described the interaction of sodium 1,8 di hydroxy 2-2 hydroxy azo benzene - 3,6 naphthalene with magnesium ions.

Sommer and Hnilickova have reviewed the analytical applications of azo chromotrope dyes and have mentioned the use and characteristic of compounds of the following type



where (R= H, - SO_3, H, - COOH, - NO_2, - OH - OM etc.

The use of hydroxy benzene azo chromotropic acid for the determination of calcium and magnesium has been recommended

by Kuznecov.[5] The use of p - hydroxy benzene azo chromotropic acid (chromotrope 10B) as a metal indicator in the determination of Th has been suggested by Schwarzenback[6].

p - nitrobenzene azochromotropic acid or 4,5 di hydroxy -3 (p - nitrophenyl azo) - 2,7 naphthalene di sulphonic acid commercially known as chromotrope 2B also belongs to the above type of compounds has long been used as the colorimetric reagent for boric acid[7] and also as a dyeing and coupling constituent for azo dyes used for cotton and wool. The reaction of this complexing agent with a number of metal ions e.g. Tl^{+3}[8] Cr^{2+}[9] and Th (iv)[10] has also been mentioned. Its use as a metal indicator in the determination of Th with E.D.T.A. has been recently reported.[11]

From what has been said above, it is clear that the work on metal - chromotrope 2B interaction lacks in information regarding the nature and composition of the coordination compounds formed. Although much has been done as far as the case of the compound as an analytical reagent is concerned. It was, therefore, thought worthwhile to carry out a few studies on this aspect of the problem. The present chapter deals with the physico - chemical studies on the cupric chloride and chromotrope 2B reaction.

Cupric chloride interacts with chromotrope 2B to form a violet coloured complex. Its composition has been determined

spectrophotometrically by employing Job's method of continuous variation and slope ratio method[13] . The results obtained by the spectrophotometric methods have been confirmed by polarography.

E X P E R I M E N T A L

Cupric chloride (AnalaR) was used during the experiments. A 1 x 10^{-2}M solution of the product was prepared by dissolving 1.7044g of the substance in one litre of doubly distilled water. Aquaous solutions of chromotrope 2B of concentration 1 x 10^{-3}M was prepared by dissolving 0.5134 gm of the B.D.H. (reagent grade) product in 1 litre of doubly distilled water.

Phosphate buffers (mixture of di sodium hydrogen phosphate and mono sodium di hydrogen phosphate, and mixture of di sodium hydrogen phosphate and caustic soda) of pH range 5.5 to 11.0 were prepared[14] from A.R. products and pH's of the solutions were checked by Beckman pH meter using a general utility glass electrode for pH values upto 10 and Beckman E type electrode for pH values above 10.

Spectrophotometric studies on Cu(ii) - Chromotrope 2B Complex

The spectrophotometric measurements were carried out using Bausch and Lomb spectronic 20' and was used after giving sufficient warming up period.

Preliminary experiments showed that cupric chloride formed a violet coloured soluble complex with chromotrope 2B in dilute solutions. The Beer's law was found to hold good for solutions having concentration below 1×10^{-3} M.

The method of Vosburgh and Cooper[15] was applied to determine the number of complexes formed in the aqueous solution. Mixtures containing equimolar solutions (1×10^{-4} M) of cupric chloride and chromotrope 2B in varying ratio (1:9, 2:8, 3:7, 4:6, 5:5 and 6:4) were prepared and their absorbances were measured at different wavelengths (in the wavelength range of 350 to 650 mu).

Concentration of $CuCl_2$ = 1 x 10^{-4}M

Concentration of Chromotrope 2B = 1 x 10^{-4}M

Wave length mu	Chromotrope 2 x 10^{-5} 2B M	2 : 8	3 : 7	4 : 6	5 : 5	6 : 4
	1	2	3	4	5	6
350	0.64	0.54	0.48	0.43	0.37	0.28
370	0.58	0.54	0.44	0.43	0.35	0.36
390	0.50	0.46	0.34	0.30	0.27	0.19
410	0.52	0.47	0.37	0.34	0.30	0.22
430	0.60	0.52	0.42	0.38	0.32	0.24
450	0.64	0.55	0.45	0.42	0.34	0.26
475	0.80	0.68	0.55	0.50	0.40	0.42
500	1.30	1.0	0.82	0.75	0.62	0.48
525	1.80	1.40	1.10	0.95	0.78	0.60
535	1.60	1.40	1.10	1.0	0.80	0.64
545	1.60	1.50	1.10	1.0	0.80	0.65
550	1.50	1.40	1.20	1.10	0.84	0.66
560	1.40	1.40	1.1	1.0	0.80	0.64
565	1.40	1.30	1.1	0.95	0.80	0.60
570	1.40	1.10	0.95	0.85	0.72	0.56
575	1.40	1.20	0.870	0.80	0.65	0.52
580	1.20	1.00	0.85	0.75	0.62	0.48
585	1.10	0.90	0.76	0.70	0.58	0.430
590	0.95	0.85	0.71	0.65	0.54	0.420
600	0.76	0.68	0.58	0.53	0.45	0.320
625	0.45	0.42	0.34	0.32	0.26	0.20
650	0.30	0.25	0.20	0.18	0.12	0.08

Fig. 1, Curve 1, 2, 3, 4, 5 and 6.

Job's method of continuous variation was employed for determining the composition of the complex. Four sets of mixtures were prepared according to the following scheme.

Set I.

Equimolar solutions of cupric chloride and chromotrope 2B of concentration 2 x 10^{-4}M were prepared and mixed in the following order:

1 cc, 2 cc, 3 cc, 4 cc, 5 cc, 6 cc, 7 cc, 8 cc and 9 cc of cupric chloride were mixed with 9 cc, 8 cc, 7 cc, 6 cc, 5 cc, 4 cc, 3 cc, 2 cc and 1 cc of chromotrope 2B respectively. The O.D. of the above mixtures were measured at 550 mu. Chromotrope 2B (2 x 10^{-5}M) was mixed with water in the following order:

1 cc, 2 cc, 3 cc, 4 cc, 5 cc, 6 cc, 7 cc, 8 cc, and nd 9 cc of chromotrope 2B were mixed with 9 cc, 8 cc, 7 cc, 6 cc, 5 cc, 4 cc, 3 cc, 2 cc, and 1 cc of water and their O.D. was measured at 550 mu.

The O.D. of the cupric chloride was found to be negligible at this concentration.

Set II.

Equimolar solutions of cupric chloride and chromotrope 2B of concentration 1 x 10^{-4}M were mixed in the same order as in Set I. chromotrope 2B (1 x 10^{-4}M) was also mixed with water in exactly the same order as in Set I.

Set III.

Equimolar solutions of cupric chloride and chromotrope 2B of concentration 5×10^{-5}M, mixed in the same order as in Set I.

Set IV.

Equimolar solutions of cupric chloride and chromotrope 2B of concentration 6.6×10^{-5}M mixed in the same order as in Set I.

The difference in O.D. (chromotrope 2B and the complex was plotted against Cu^{ii} / Cu^{ii} + chromotrope 2B

Table 2.

Set I.

Wavelength: 550 mu

Vol. of $CuCl_2$	Vol. of Chromotrope 2B	O.D.	Vol. of H_2O	Vol. of Chromotrope 2B	O.D.	Diff. in O.D.
1 cc	9 cc	2.0	1 cc	9 cc	2.0	0
2 cc	8 cc	1.8	2 cc	8 cc	1.1	0.07
3 cc	7 cc	1.7	3 cc	7 cc	1.6	0.10
4 cc	6 cc	1.5	4 cc	6 cc	1.3	0.20
5 cc	5 cc	1.4	5 cc	5 cc	1.1	0.30
6 cc	4 cc	1.0	6 cc	4 cc	0.80	0.20
7 cc	3 cc	0.80	7 cc	3 cc	0.64	0.16
8 cc	2 cc	0.52	8 cc	2 cc	0.45	0.07
9 cc	1 cc	0.26	9 cc	1 cc	0.26	0

Fig. 2, Curve 1.

Table 3.

Set II.

Wavelength : 550 mu

Vol. of $CuCl_2$	Vol. of Chromotrope 2B	O.D.	Vol. of H_2O	Vol. of Chromotrope 2B	O.D.	Diff. in O.D
1 cc	9 cc	1.0	1 cc	9 cc	1.0	0
2 cc	8 cc	0.90	2 cc	8 cc	0.88	0.02
3 cc	7 cc	0.85	3 cc	7 cc	0.80	0.05
4 cc	6 cc	0.71	4 cc	6 cc	0.64	0.07
5 cc	5 cc	0.64	5 cc	5 cc	0.54	0.10
6 cc	4 cc	0.58	6 cc	4 cc	0.50	0.08
7 cc	3 cc	0.34	7 cc	3 cc	0.29	0.05
8 cc	2 cc	0.22	8 cc	2 cc	0.20	0.02
9 cc	1 cc	0.11	9 cc	1 cc	0.16	0

Fig. 2, Curve 2.

Table 4.

Set III.

Wave length : 550 mu

Vol. of $CuCl_2$	Vol. of Chromotrope 2B	O.D.	Vol. of H_2O	Vol. of Chromotrope 2B	O.D.	Diff. in O.D.
1 cc	9 cc	0.60	1 cc	9 cc	0.60	0
2 cc	8 cc	0.58	2 cc	8 cc	0.59	0.01
3 cc	7 cc	0.52	3 cc	7 cc	0.50	0.02
4 cc	6 cc	0.47	4 cc	6 cc	0.42	0.05
5 cc	5 cc	0.40	5 cc	5 cc	0.33	0.07
6 cc	4 cc	0.30	6 cc	4 cc	0.26	0.04
7 cc	3 cc	0.21	7 cc	3 cc	0.18	0.03
8 cc	2 cc	0.14	8 cc	2 cc	0.13	0.01
9 cc	1 cc	0.11	9 cc	1 cc	0.11	0

Fig. 1

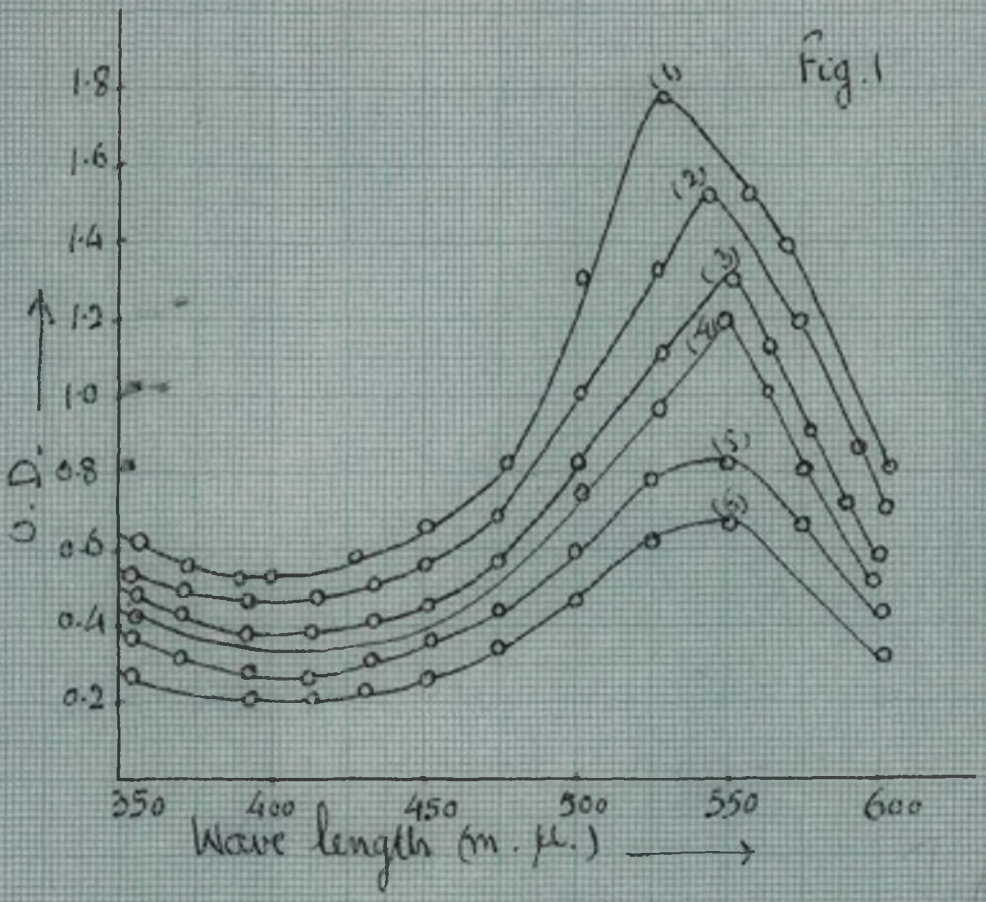

1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
O. D.
(1)
(2)
(3)
(4)
(5)
(6)
350
400
450
500
550
600
Wave length (m. μ.) ⟶

Fig. 2.

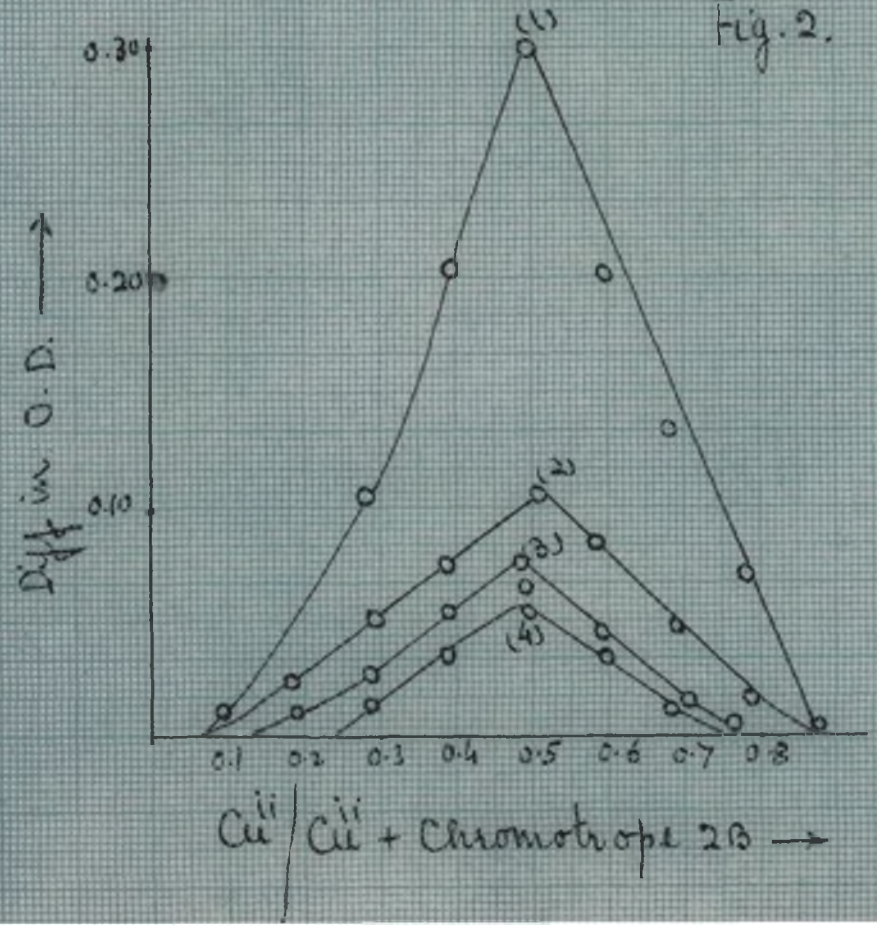

0·30
0·20
0·10
Diff. in O. D.
(1)
(2)
(3)
(4)
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
Cu++ / Cu++ + Chromotrope 2B ⟶

Table 5.

Set IV.

Wave length : 550 mu

Vol. of $CuCl_2$	Vol. of Chromotrope 2B	O.D.	Vol. of H_2O	Vol. of Chromotrope 2B	O.D.	Diff. in O.D.
1 cc	9 cc	0.45	1 cc	9 cc	0.45	0
2 cc	8 cc	0.45	2 cc	8 cc	0.45	0
3 cc	7 cc	0.37	3 cc	7 cc	0.35	0.01
4 cc	6 cc	0.33	4 cc	6 cc	0.30	0.03
5 cc	5 cc	0.31	5 cc	5 cc	0.26	0.05
6 cc	4 cc	0.26	6 cc	4 cc	0.22	0.04
7 cc	3 cc	0.17	7 cc	3 cc	0.16	0.01
8 cc	2 cc	0.11	8 cc	2 cc	0.11	0
9 cc	1 cc	0.12	9 cc	1 cc	0.12	0

Fig. 2, Curve 4.

The composition of the complex was further investigated by employing the slope ratio method. Two sets of experiments were performed. In the first set the concentration of chromotrope 2B was kept constant; in the other set the mixing was done in reverse order.

Fig. 4.

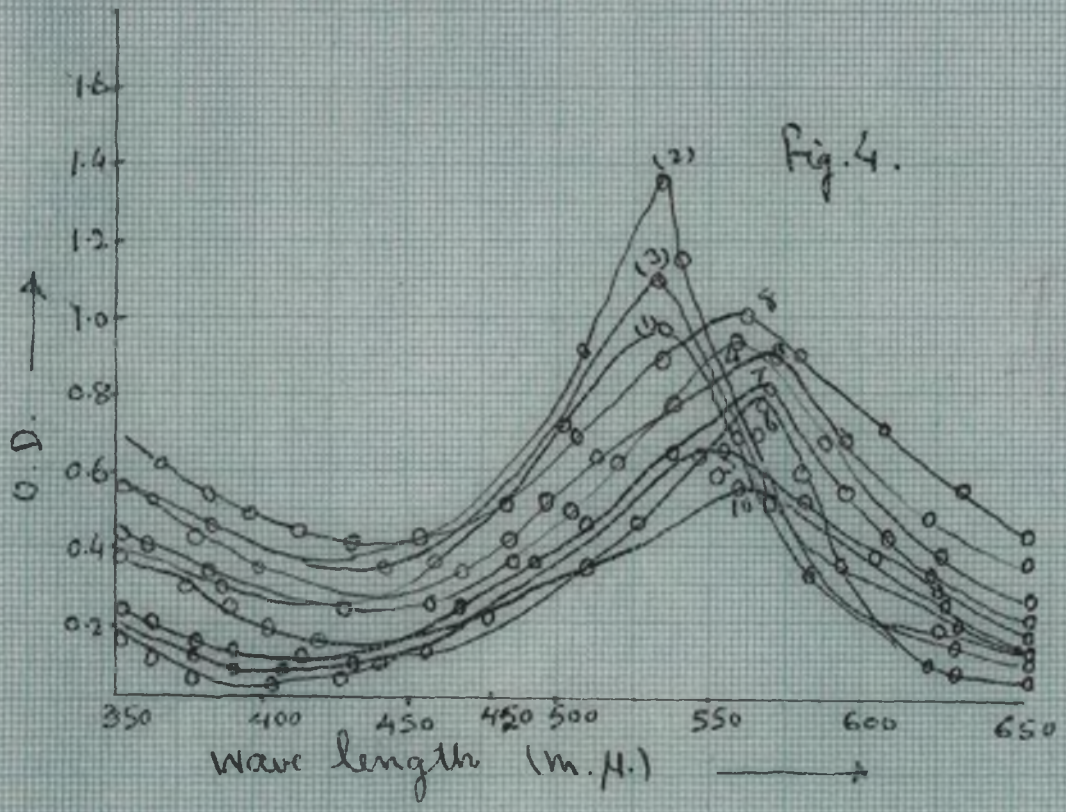

O.D.
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
350
400
450
500
550
600
650
Wave length (m.μ.)

Fig. 3

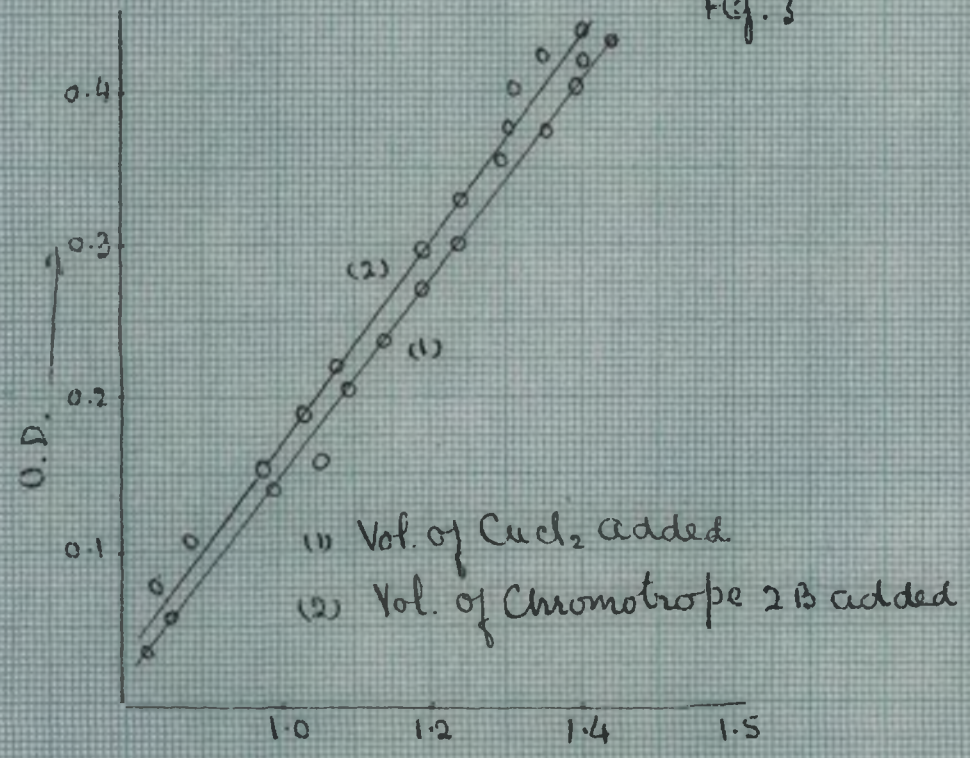

O.D.
0.4
0.3
0.2
0.1
1.0
1.2
1.4
1.5
(1) Vol. of $CuCl_2$ added
(2) Vol. of Chromotrope 2B added

Table 6.

Set I.

Volume of 5×10^{-4} M chromotrope 2B = 0.5 cc

Strength of $CuCl_2$ = 1×10^{-4} M

Wave length : 550 mu

Set II.

Volume of 5×10^{-4} M $CuCl_2$ = 0.5 cc

Strength of chromotrope 2B = 1×10^{-4} M

Wave length : 550 mu

The solutions were diluted to 10 cc before the O.D. measurements were made.

Set I		Set II	
Volume of $CuCl_2$ added	O.D.	Volume of Chromotrope 2B added	O.D.
0.0 cc	-	0.0 cc	0.03
0.2 cc	0.02	0.2 cc	0.075
0.4 cc	0.05	0.4 cc	0.08
0.5 cc	0.05	0.5 cc	0.10
1.0 cc	0.13	1.0 cc	0.16
1.2 cc	0.155	1.2 cc	0.18
1.4 cc	-	1.4 cc	0.225
1.5 cc	0.20	1.5 cc	0.225
2.0 cc	0.27	2.0 cc	0.29
2.5 cc	0.33	2.5 cc	0.35
3.0 cc	0.40	3.0 cc	0.44

Fig. 3, Curve 1, 2.

The absorbances of the equimolar mixtures (1×10^{-5}M) of cupric chloride and chromotrope 2B were measured at different wave lengths from 350 to 650 mu in the pH range 4 to 11.5, using Walpole acetate buffers, Na_2HPO_4 - NaH_2PO_4, and Na_2HPO_4 - NaOH buffers prepared from AnalaR reagents.

Table 7.

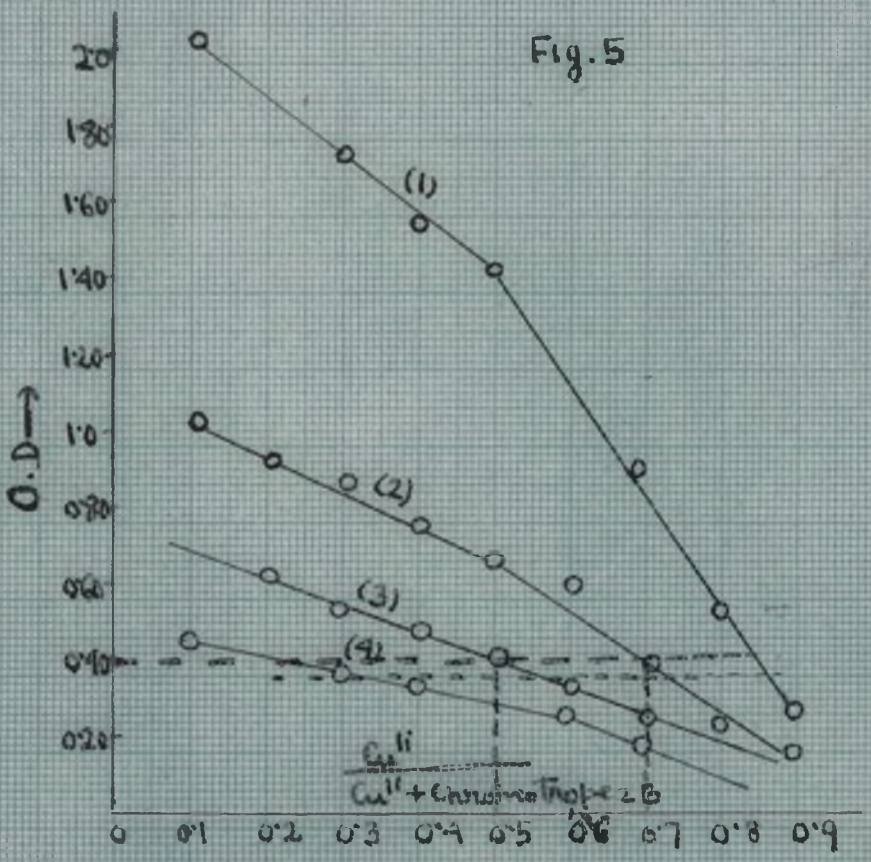
Concentration of $CuCl_2$ = 1×10^{-4}M

Concentration of chromotrope 2B = 1×10^{-4}M

Wave length in mu	pH = 4.3	pH = 5.5	pH = 6.6	pH = 7.0	pH = 7.5	pH = 8.9	pH = 10.6	pH = 11.0	pH = 11.
	1	2	3	4	5	6	7	8	9
350	0.33	0.54	0.53	0.44	0.45	0.24	0.53	0.78	0.20
360	0.32	0.50	0.51	0.38	0.38	0.20	0.50	0.62	0.14
375	0.30	0.42	0.42	0.34	0.28	0.18	0.44	0.44	0.10
385	0.30	0.42	0.40	0.36	0.24	0.14	0.40	0.48	0.08
400	0.25	0.38	0.35	0.28	0.18	0.14	0.30	0.46	0.08
410	0.24	0.38	0.34	0.26	0.14	0.12	0.31	0.44	0.09
425	0.24	0.36	0.33	0.22	0.14	0.13	0.30	0.42	0.09
450	0.32	0.42	0.38	0.24	0.08	0.21	0.32	0.42	0.10
475	0.50	0.58	0.56	0.36	0.24	0.30	0.38	0.50	0.20
500	0.80	0.90	0.84	0.52	0.40	0.44	0.65	0.60	0.30
515	0.93	1.1	1.0	0.62	0.54	0.56	0.72	0.80	0.40
525	0.98	1.4	1.1	0.72	0.60	0.64	0.75	0.90	0.52
550	0.72	0.82	0.75	0.84	0.64	0.82	0.85	1.0	0.78
560	0.62	0.60	0.60	0.90	0.62	0.70	0.80	0.98	0.64
575	0.50	0.35	0.41	0.78	0.52	0.66	0.66	0.84	0.60
600	0.340	0.22	0.30	0.52	0.40	0.42	0.43	0.70	0.42
625	0.22	0.16	0.22	0.38	0.28	0.30	0.28	0.54	0.30
650	0.12	0.10	0.18	0.30	0.18	0.34	0.30	0.46	0.28

Fig. 4, Curve 1, 2, 3, 4, 5, 6, 7, 8, and 9.

Fig. 5


O.D
2·0
1·80
1·60
1·40
1·20
1·0
0·80
0·60
0·40
0·20
(1)
(2)
(3)
(4)
Cu I
Cu II + Chromatrope 2B
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9

For determining the formation constant of the complex, Four sets of mixtures with concentration of the reactants as 2×10^{-4}M, 1×10^{-4}M, 5×10^{-5}M and 6.66×10^{-5}M were prepared according to Job's method of continuous variation (Table 2, 3, 4 and 5) the O.D. of the mixtures were measured at 550mu and was plotted against Cu^{ii}/Cu^{ii} + chromotrope 2B

Table 8.

		Set I, Conc. $2x10^{-4}$M	Set II Conc. $1x10^{-4}$M	Set III Conc. $5x10^{-5}$M	Set IV Conc. $6.66x10^{-5}$M
Vol. of $CuCl_2$	Vol. of Chromotrope 2B	O.D.	O.D.	O.D.	O.D.
1 cc	9 cc	2.0	1.0	0.45	0.60
2 cc	8 cc	1.80	0.90	0.45	0.58
3 cc	7 cc	1.70	0.85	0.37	0.52
4 cc	6 cc	1.50	0.71	0.33	0.47
5 cc	5 cc	1.40	0.64	0.31	0.40
6 cc	4 cc	1.0	0.58	0.26	0.30
7 cc	3 cc	0.80	0.34	0.17	0.21
8 cc	2 cc	0.52	0.22	0.11	0.14
9 cc	1 cc	0.26	0.16	0.12	0.11

Fig. 5, Curve 1, 2, 3 and 4.

The value of K, the formation constant is given by the equation.

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

$$\text{Or} \quad x = \frac{a_1 b_1 - a_2 b_2}{(a_1 - b_1) - (a_2 - b_2)}$$

Where x is the concentration of complex at the equilibrium a_1 and a_2 and b_1 and b_2 are the concentrations of the reactants giving the same O.D.

The values of a_1, b_1 and a_2, b_2 found from the curves are

$a_1 = 5.0 \times 6.6 \times 10^{-5}M$ $\quad b_1 = 5.0 \times 6.6 \times 10^{-5}M$

$a_2 = 7.0 \times 1.0 \times 10^{-4}M$ $\quad b_2 = 3.0 \times 1.0 \times 10^{-5}M$

at the same O.D. of 0.40.

Polarographic Studies on Cu(ii) - Chromotrope 2B complex

The polarographic measurements were made using the Fischer electropode in conjunction with a multiflex galvanometer MGF2 in the external circuit. The inert atmosphere in the cell was maintained by bubbling nitrogen after passing it through alkaline pyragallol and chromous chloride solution. Methyl red of concentration 0.001 % and KCl (AnalaR) solution were used as maximum suppressor and supporting electrolyte respectively. All measurements were carried at 30 $\pm$ 0.1°C.

Cupric chloride solution of concentration $1 \times 10^{-2}M$ and chromotrope 2B (sodium salt) of concentration $2 \times 10^{-3}M$ were prepared for polarographic studies. Polarograms were taken in buffers of pH ranging 7.0 to 11.5 (using phosphate buffers prepared from A.R. products) and their pH's were checked with Beckman pH meter model G using a general utility

Beckman glass electrode for pH values upto 10 and Beckman E glass electrode for higher values above 10.

As a whole about twenty polarograms were studied. Typical polarograms are given in Fig. 6 and 7.

Table 9.

Set I. 0.0 cc Cu^{ii} + 2 cc methyl red (1×10^{-3}%) + 10 cc KCl(2M) + 10 cc Chromotrope 2B (2×10^{-3}M) + 8 cc buffer (pH = 7.5).

Set II. (i) 0.5 cc Cu^{ii} (1×10^{-2}M) + 2 cc methyl red (1×10^{-3}%) + 10 cc KCl (2M) + 10 cc Chromotrope 2B (2×10^{-3}M) 8.0 cc buffer - pH = 7.5

(ii) 0.5 cc Cu^{ii} (1×10^{-2}M) + 2 cc methyl red (1×10^{-3}%) + 10 cc KCl (2M) + 10 cc Chromotrope (2B) (2×10^{-3}M) + 7.5 cc buffer - pH = 7.5

(iii) 0.5 cc Cu^{ii} (1×10^{-2}M) + 2 cc methyl red (1×10^{-3}% + 10 cc KCl (2M) + 12 cc Chromotrope 2B (2×10^{-3}M) + 5.5 cc buffer (pH = 7.5).

(iv) 0.5 cc Cu^{ii} (1×10^{-2}M) + 2 cc methyl red (1×10^{-3}%) + 10 cc KCl (2M) + 14 cc Chromotrope 2B + 3.5 cc buffer (pH = 7.5).

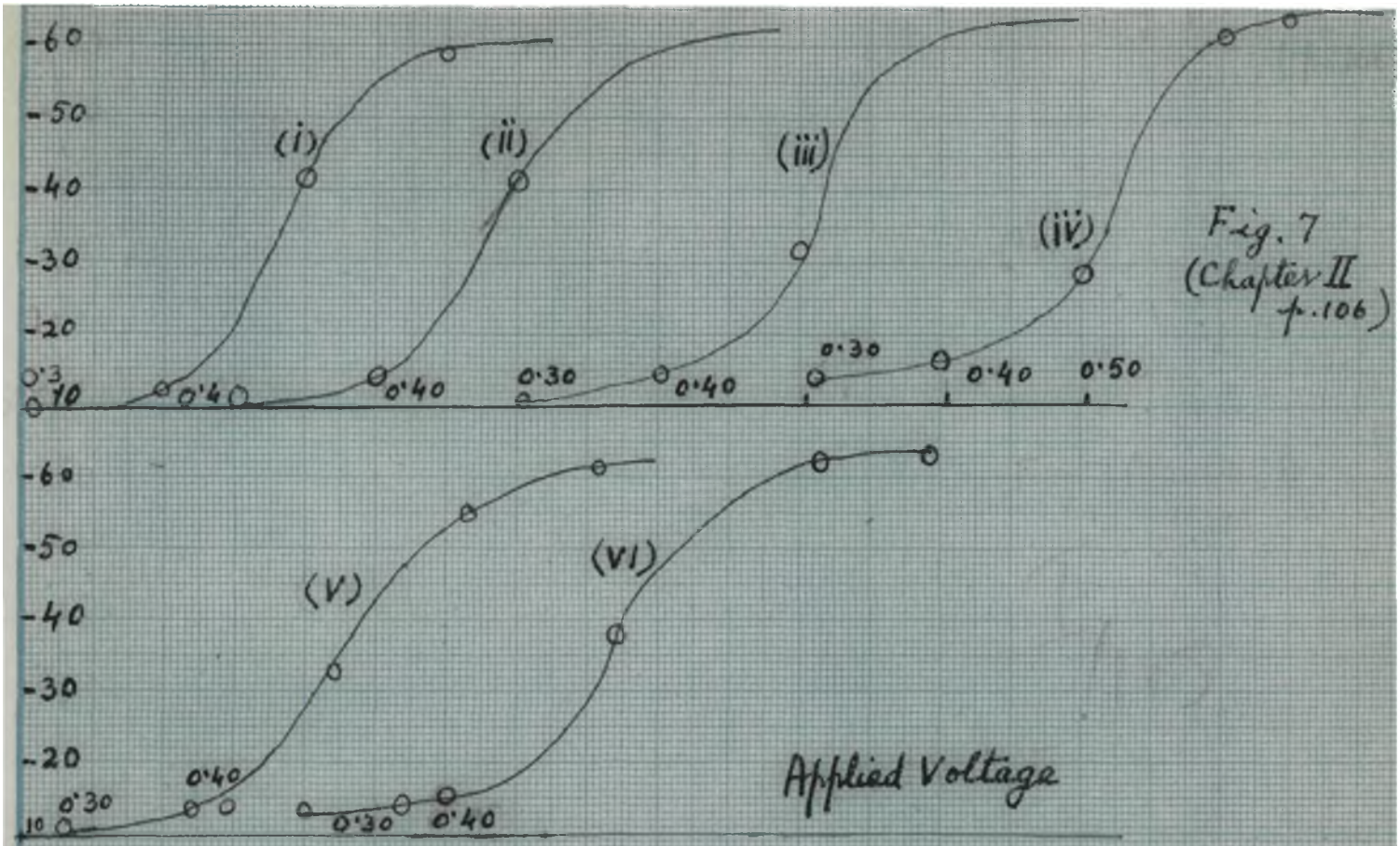


Fig. 7
(Chapter II
p. 106)

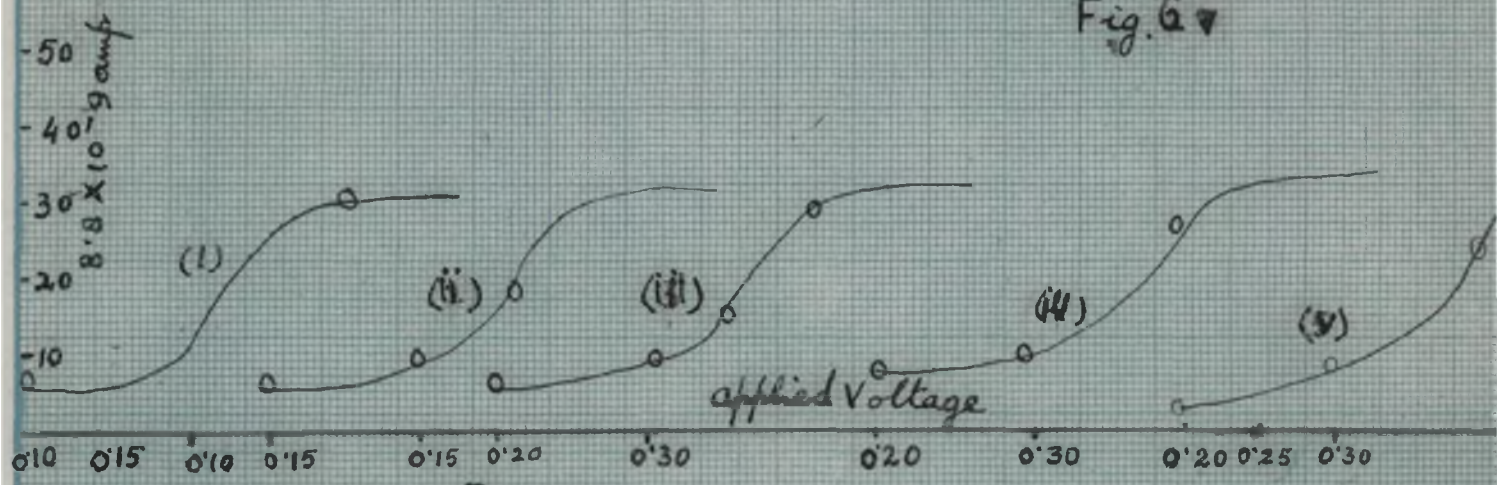


Fig. 6

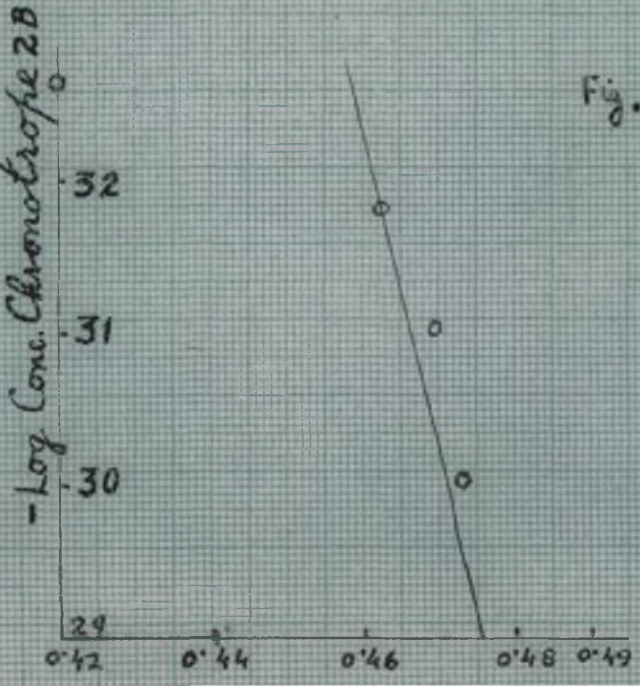


Fig. 8

(v) 0.5 cc Cu^{ii} (1 x 10^{-2}M) + 2 cc methyl red (1x10^{-3}%) + 10 cc KCl(2M) + 16 cc Chromotrope 2B + 1.5 cc buffer (pH = 7.5).

Applied potential in Volts.	Current (8.8 x 10^{-9} ampere)				
	0 (i)	6.6x10^{-4}M (ii)	8x10^{-4}M (iii)	9.3x10^{-4}M (iv)	1.25x10^{-3}M (v)
0	6.0	6.0	6.5	6.5	6.5
0.3	6.0	7.0	6.5	8.0	4.0
0.35	6.0	7.0	7.0	8.5	5.5
0.40	10.0	9.0	9.0	9.0	10.0
0.45	25.0	14.0	14.0	14.0	12.0
0.50	30.0	28.0	28.0	24.5	25.0
0.55	30.0	28.5	30.0	30.0	30.0
0.60	30.5	29.0	31.0	31.5	30.5
0.65	30.5	30.0	31.0	32.0	30.5
0.70	30.5	30.5	31.0	32.0	30.5
0.80	30.5	31.0	31.0	32.0	30.5

Fig. 6, Curve i, ii, iii, iv, and v.

Table 10.

Set II.

(i) 1.0 cc Cu^{ii} (1 x 10^{-2}M) + 2 cc methyl red (1 x 10^{-3}%) + 10 cc KCl (2M) + 10 cc Chromotrope 2B (2 x 10^{-3}M) + 12 cc buffer (11.5)

(ii) 1.0 cc Cu^{ii} (1 x 10^{-2}M) + 2 cc methyl red (1 x 10^{-3}%) + 10 cc KCl (2M) + 12 cc Chromotrope 2B (2 x 10^{-3}M) + 10 cc buffer (11.5).

(iii) 1.0 cc Cu^{ii} (1 x 10^{-2}M) + 2 cc methyl red (1 x 10^{-3}%
+ 10 cc KCl (2M) + 14 cc Chromotrope 2B (2 x 10^{-3}M)
+ 8 cc buffer (pH = 11.5).

(iv) 10 cc Cu^{ii} (1 x 10^{-2}M) + 2 cc methyl red (1x10^{-3}%)
+ 11 cc KCl (2M) + 16 cc Chromotrope 2B (2x10^{-3}M)
+ 6 cc buffer (pH = 11.5)

(v) 1.0 cc Cu^{ii} (1 x 10^{-2}M) + 2 cc methyl red (1x10^{-3}%)
+ 10 cc KCl (2M) + 18 cc Chromotrope 2B (2x10^{-3}M)
+ 4 cc buffer (pH = 11.5).

(vi) 1.0 cc Cu^{ii} (1 x 10^{-2}M) + 2 cc methyl red
(1 x 10^{-3}%) + 10 cc KCl (2M) + 20 cc Chromotrope 2B
(2 x 10^{-3}M) + 2 cc buffer (pH = 11.5).

Applied potential (in Volts)	Current(8.8×10^{-9} ampere)					
	5.7×10^{-4} (i)	6.6×10^{-4} (ii)	8.0×10^{-4} (iii)	9.5×10^{-4} (iv)	1.1×10^{-3} (v)	1. 10 1 (v
0	7.0	7.0	7.0	7.0	6.0	6.5
0.3	11.5	11.5	11.5	12.5	13.5	13.75
0.35	12.0	11.5	12.0	13.5	14.5	14.0
0.40	12.5	12.5	14.0	14.0	15.0	15.5
0.45	22.5	24.0	18.0	18.0	20.5	16.0
0.50	42.0	40.0	30.0	27.5	34.0	20.0
0.55	55.0	52.5	52.0	51.5	46.0	36.5
0.60	59.0	58.0	60.0	58.0	54.5	49.5
0.65	59.5	60.0	60.5	59.5	59.0	57.5
0.70	59.5	60.0	61.0	60.0	60.0	60.0
0.75	59.5	60.0	61.0	60.0	60.0	60.5
0.80	59.5	60.0	61.0	60.0	60.0	60.5

Fig. 7, Curve i, ii, iii, iv, v and vi.

D I S C U S S I O N

The results on spectrophotometric and polarographic studies on the interaction of cupric chloride and chromotrope 2B present the following interesting features regarding the composition of the complex.

Spectrophotometric studies:

On applying Vosburgh and Cooper's method for the mixtures (containing reactants each of concentration 1 x 10^{-4}M mixed in the ratio Cu^{++}: Chromotrope 2B as 2:8, 3:7, 4:6, 5:5 and 6:4) only one maxima at 550 mu was obtained, showing thereby the existence of only one complex (Table 1, Fig. 1).

Job's method of continuous variation (carried out at the wave length 550 mu) applied to the four different sets of concentration (2 x 10^{-4}M, 1 x 10^{-4}M, 6.6 x 10^{-5}M and 5 x 10^{-4}M) gave a combining ratio of 1:1 for Cu^{++} to Chromotrope 2B (Fig. 2, Table 2, 3, 4 and 5).

Also, the above results found support from slope ratio method (Fig. 3, Table 6) where from the slope of the straight line portion of curve the same combining ratio of 1:1 was obtained.

The formation constant was determined by the same method as described in Chapter I, page 49. For two

concentrations of Cu^{++} and Chromotrope 2B (a_1 = 5.0 x 6.6 x 10^{-5}M a_2 = 7.0 x 1.0 x 10^{-4}M and b_1 = 5.0 x 6.6 x 10^{-5}M, b_2 = 3.0 x 1.0 x 10^{-5}M) at the same O.D. (0.40: Fig. 5, Table 8), the value of K was found to be 2.11 x 10^6 and that of free energy - ΔF^o = 4.22 K Cals.

Polarographic Studies:

Polarograms in different pH media (7.5 and 11.5) show that the reduction of the cupric chromotrope 2B complex is reversible at the dropping electrode with transfer of one electron as the values of $E_{3/4} - E_{1/4}$ (Tomes method)[16] were found to be between 0.05 and 0.06. The following are the $E_{1/2}$ values at different concentration of chromotrope 2B.

Table 11.

Concentration of $CuCl_2$ = 1.66 x 10^{-4}M

Conc. of Chromotrope 2B	- log Conc. of chromotrope 2B	$E_{1/2}$ (pH = 7.5)
6.6 x 10^{-4}M	3.176	0.465
8 x 10^{-4}M	3.096	0.470
9.3 x 10^{-4}M	3.029	0.475
1.25x 10^{-4}M	2.903	0.450

Fig. 8, Curve 1.

Table 12.

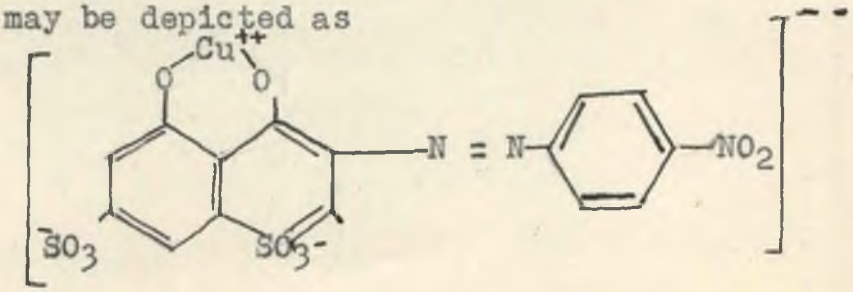
Concentration of $CuCl_2$ = 2.85×10^{-4}M

Conc. of Chromotrope 2B	- log Conc. of chromotrope 2B	$E_{1/2}$ (pH = 11.5)
5.7×10^{-4}M	3.24	0.505
6.6×10^{-4}M	3.17	0.515
8.0×10^{-4}M	3.09	0.520
9.5×10^{-4}M	3.02	0.525
1.0×10^{-3}M	3.00	0.531
1.1×10^{-3}M	2.94	0.535

Fig. 8, Curve 2.

The straight lines obtained by plotting $E_{1/2}$ values against - log conc. of chromotrope 2B for pH = 11.5 and 6.5 (Fig. 8) gave a slope of 0.05, which shows that one chromotrope 2B molecule combines with one Cu^{++} atom.

On the basis of the information obtained from spectrophotometric and polarographic studies the formula of the complex may be depicted as



From the foregoing results it may be concluded that chromotrope 2B can be used for the detection of cupric ions present in very minute quantities, also, it may be used a colorimetric reagent for Cu^{ii} ions in solutions. The most favourable conditions for using this reagent should be (i) concentration of Cu^{++} ions in the range of(2×10^{-4}M to 1×10^{-6}M). (ii) the pH of the medium should be in the range of 7.5 to 11.5.

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C H A P T E R III.

Interaction of Vanadyl ions with 8, Hydroxy Quinoline 7 Iodo 5 Sulphonic Acid (Ferron).

INTERACTION OF VANADYL IONS WITH 8, HYDROXY QUINOLINE 7 IODO 5 SULPHONIC ACID (FERRON).

The importance of 8, hydroxy quinoline and its substituted compounds is well established in the field of analytical chemistry.[1] The strong complex forming capability of these compounds has been attributed to the presence of -OH substituted quinoline ring which facilitates the possibility of coordination through hydroxyl group and nitrogen and thus forming stable coordination compounds.[2] 8, hydroxy quinoline 7 iodo 5 sulphonic acid, better known as Ferron, also belongs to such type of compounds. It was used for a long time as a colorimetric reagent for iron.[3] But recently its reactions with other metals like Bi[4], Tl[5], Co[6] etc. were also reported and in connection with the detection and determination of these metal ions.

Tenvo Nortia investigated the structure and bonding in cobalt chelate by employing spectrophotometric and magnetic susceptibility measurements. According to his findings the compound Na_2 (Co^{ii} ($C_9H_4O_4NIS)_2$) has covalent bonds, square planar structure and thus having a coordination No. 4. Ferron has also been employed in the separation of plutonium from Uranium and other fission products.[7] Eugne L. Colichman and others[8] have investigated the polarographic properties of Ferron in terms of Hammet's Linear Free Energy Relation between structure and reactivity. Most substituents in the o-position to the iodogroup yield abnormal half wave potentials. The

proximity phenomenon facilitates the polarographic reduction of the iodogroup whether the substituent is electropositive or electronegative, the value of $E_{1/2}$ calculated for Ferron (1×10^{-3}M conc.) was 1.42 volt vis S.C.E.

Keeping in view the strong coordinating property of hydroxy quinoline and its substituted compounds, and their tendency to form complexes with transitional elements, the reaction of Ferron with vanadyl sulphate was studied.

Vanadyl sulphate solution when mixed with 8, hydroxy quinoline 7 iodo 5 sulphonic acid gave a yellowish green compound. The compound was found to be quite stable and remained so over a quite large pH range. The complex was studied by employing (a) spectrophotometric and (b) conductometric methods. These investigations besides giving composition of the complex have provided a new method for the colorimetric estimation of vanadyl ions.

E X P E R I M E N T A L

Vanadyl sulphate (Riedel) was used for the experiments. Vanadyl ions were estimated[9] by the same method as described in Chapter I, page 24.

Dilute solution of 8, hydroxy quinoline 7 iodo 5 sulphonic acid (Ferron) of concentration 1 x 10^{-3}M was obtained by dissolving 0.3511g of the B.D.H. AnalaR product in 1 litre of double distilled water.

Buffer solutions in the pH range 2.0 - 11.5 were prepared by using Prideaux and Ward Universal buffer mixtures. Mixtures of 100 cc of solution containing 0.04M H_3PO_4, 0.04N - phenyl acetic acid and 0.04N - boric acid (all A.R. products) were neutralized with varying amounts of 0.2NNaOH (A.R.) giving buffer solutions of the required pH.

Spectrophotometric Studies on Vanadyl Sulphate - Ferron Complex.

Spectrophotometric measurements were carried out with Beckman D.U. Spectrophotometer with 10 m.m. corex cells Tungston lamp was used as the light source.

Before carrying out absorption experiments on the composition of the complex, Vosburgh and Cooper's[11] method

was employed to know the number of complexes formed. Equimolar solutions of vanadyl sulphate and ferron of concentration 2×10^{-3}M were mixed in the ratio 4:6, 5:5 and 6:4 respectively and their absorbances were noted at different wave lengths in the wave length range of 325 to 525 mu.

Table 1.

Concentration of Vanadyl Sulphate = 2×10^{-3}M

Concentration of Ferron = 2×10^{-3}M

Wave length mu	4 : 6 O.D.	5 : 5 O.D.	6 : 4 O.D.
	1	2	3
325	1.20	1.0	0.71
330	1.15	0.96	0.67
335	1.15	0.92	0.64
340	1.10	0.90	0.62
345	1.15	0.94	0.64
350	1.25	1.05	0.72
360	1.50	1.30	0.88
370	1.80	1.50	1.05
375	1.85	1.55	1.075
380	2.0	1.80	1.30
385	1.9	1.60	1.10
390	1.9	1.60	1.10
395	1.85	1.50	1.10
400	1.80	1.40	0.96
410	1.35	1.10	0.72
425	0.75	0.64	0.345
450	0.140	0.075	0.045
475	0.050	0.01	0.01
500	0.040	-	-
525	0.035	-	-

Fig. 1, Curve 1, 2 and 3.

Table 2.

Concentration of Ferron = 2×10^{-3}M

Wave length mu	Ferron : Water 5 : 5 O.D. (4)	Ferron : water 6 : 4 O.D. (5)
325	1.7	0.88
335	1.8	0.84
350	1.4	0.55
360	0.92	0.320
375	0.79	0.290
400	0.61	0.375
415	0.90	0.42
425	0.94	0.44
435	0.98	0.445
445	0.96	0.445
450	0.94	0.420
475	0.65	0.30
500	0.30	0.145
525	0.035	0.035

Fig. 1, Curve 4, 5.

The composition of the complex was determined by Job's method[12] of continuous variation. Mixtures of equimolar solutions of vanadyl sulphate and Ferron were mixed according to the following scheme.

Set I. Conc. of vanadyl sulphate and Ferron (1×10^{-3}M). The solutions were mixed in the following order.

1 cc, 2 cc, 3 cc, 4 cc, 5 cc, 6 cc, 7 cc, 8 cc and 9 cc of vanadyl sulphate were mixed with 9 cc, 8 cc, 7 cc, 6 cc, 5 cc, 4 cc, 3 cc, 2 cc and 1 cc of Ferron respectively and

their optical densities were noted at 380 mu.

9 cc, 8 cc, 7 cc, 6 cc, 5 cc, 4 cc, 3 cc, 2 cc and 1 cc of ferron (1×10^{-3}M) were mixed with 1 cc, 2 cc, 3 cc, 4 cc, 5 cc, 6 cc, 7 cc, 8 cc and 9 cc of water respectively and their optical densities were measured at 380 mu.

Set II. Conc. of vanadyl sulphate and Ferron = 8×10^{-4}M
all other details being the same as in Set I.

Set III. Conc. of vanadyl sulphate and Ferron = 4×10^{-4}M
all other details being the same as in Set I.

Set IV. Conc. of Vanadyl sulphate and Ferron = 2×10^{-4}M
all other details being the same as in Set I.

The O.D. of vanadyl sulphate at these concentration was found to be negligible.

Curves were plotted between the diff. in O.D. (O.D. of the complex - optical density of ferron) versus VO^{++}/VO^{++} + ferron.

Table 3.

Set I.

Concentration of Vanadyl Sulphate = 1×10^{-3}M

Concentration of Ferron = 1×10^{-3}M

Vol.of $VOSO_4$	Vol. of Ferron	O.D.	Vol. of Ferron	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	1.30	9 cc	1 cc	0.80	0.50
2 cc	8 cc	1.50	8 cc	2 cc	0.65	0.85
3 cc	7 cc	1.75	7 cc	3 cc	0.58	1.17
4 cc	6 cc	1.90	6 cc	4 cc	0.36	1.54
5 cc	5 cc	1.75	5 cc	5 cc	0.375	1.375
6 cc	4 cc	1.40	4 cc	6 cc	0.280	1.055
7 cc	3 cc	1.10	3 cc	7 cc	0.30	0.80
8 cc	2 cc	0.76	2 cc	8 cc	0.165	0.595
9 cc	1 cc	0.380	1 cc	9 cc	0.080	0.30

Fig. 2, Curve 1.

Table 4.

Set II.

Concentration of Vanadyl Sulphate = 8×10^{-4}M

Concentration of Ferron = 8×10^{-4}M

Vol. of $VoSO_4$	Vol. of Ferron	O.D.	Vol. of Ferron	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	1.15	9 cc	1 cc	0.83	0.32
2 cc	8 cc	1.25	8 cc	2 cc	0.69	0.56
3 cc	7 cc	1.60	7 cc	3 cc	0.82	0.78
4 cc	6 cc	1.70	6 cc	4 cc	0.70	1.0
5 cc	5 cc	1.60	5 cc	5 cc	0.76	0.84
6 cc	4 cc	1.35	4 cc	6 cc	0.67	0.68
7 cc	3 cc	1.00	3 cc	7 cc	0.46	0.54
8 cc	2 cc	0.90	2 cc	8 cc	0.52	0.38
9 cc	1 cc	0.75	1 cc	9 cc	0.55	0.20

Fig. 2, Curve 2.

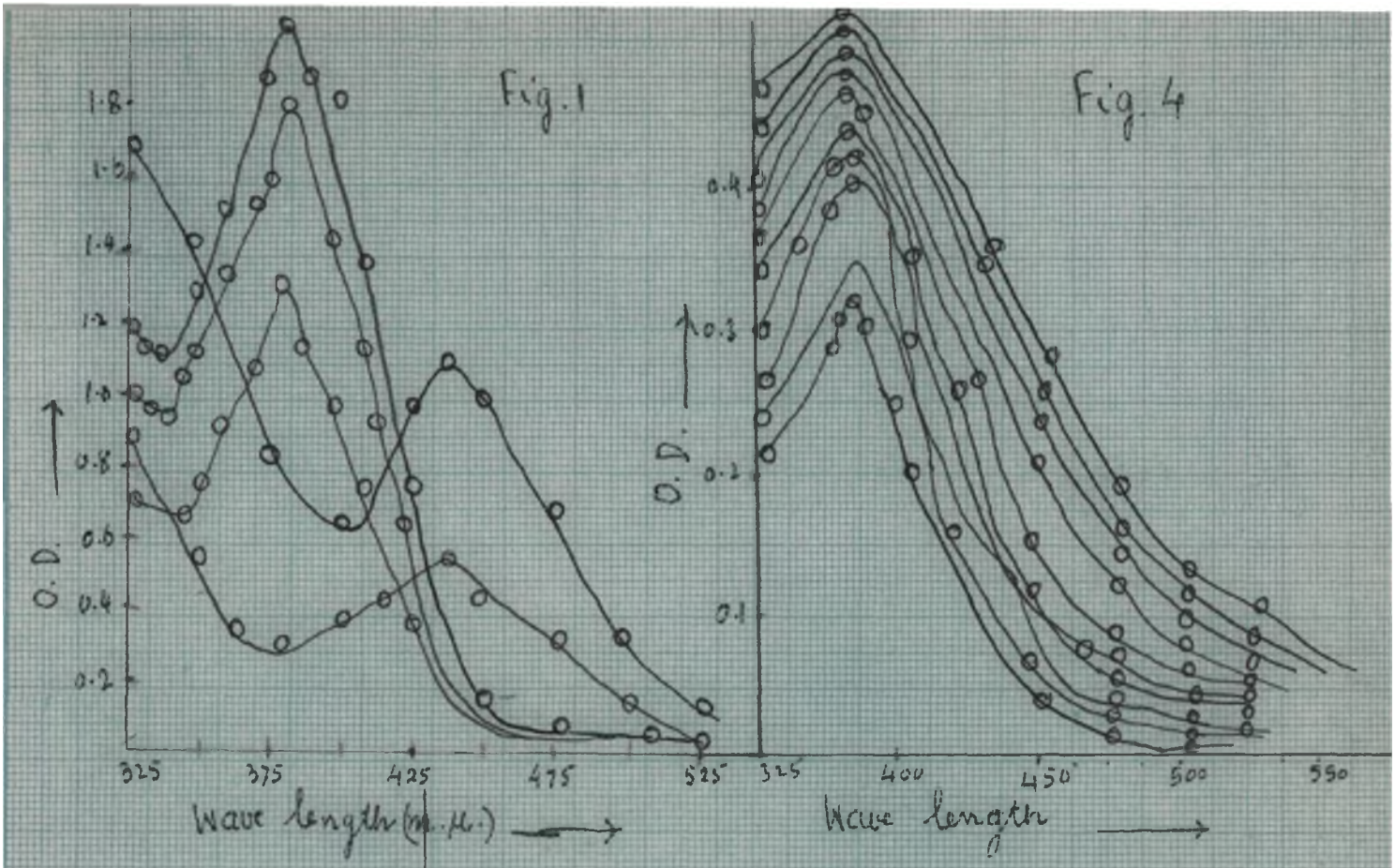


Fig. 1
O.D.
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
325
375
425
475
525
Wave length (m.μ.)

Fig. 4
O.D.
0·4
0·3
0·2
0·1
325
400
450
500
550
Wave length

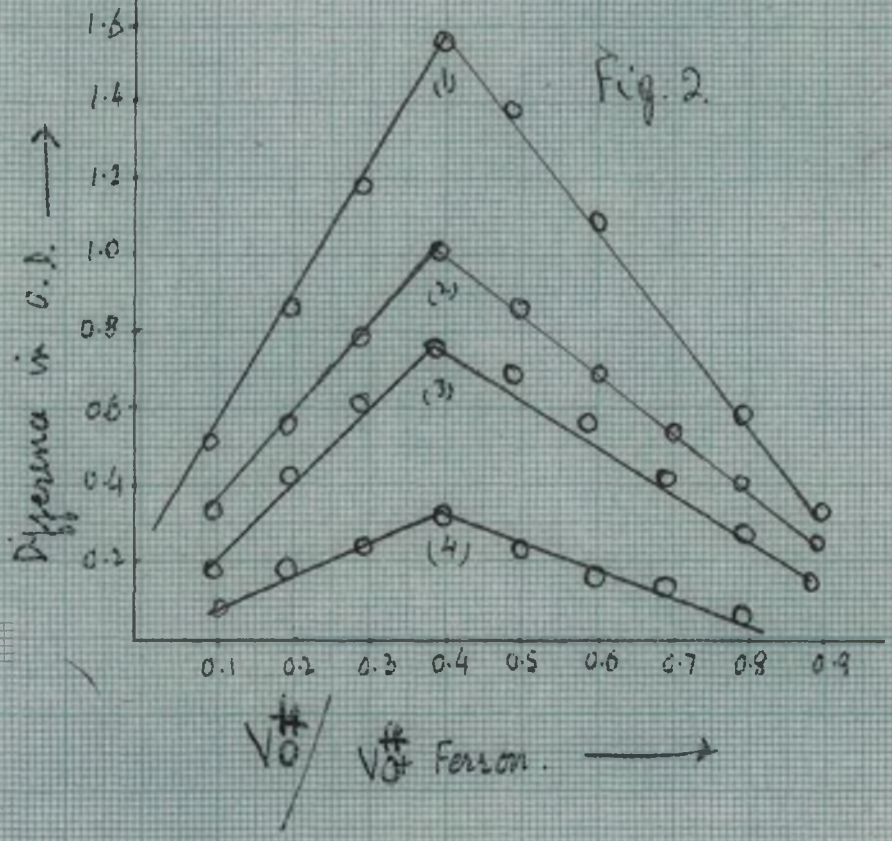


Fig. 2.
Difference in O.D.
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
(1)
(2)
(3)
(4)
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
V0 / Vσ Ferron.

Table 5.

Set III.

Concentration of Vanadyl Sulphate = 4×10^{-4}M

Concentration of Ferron = 4×10^{-4}M

Wave length: 380 mu

Vol. of $VOSO_4$	Vol. of Ferron	O.D.	Vol. of Ferron	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.53	9 cc	1 cc	0.355	0.1715
2 cc	8 cc	0.72	8 cc	2 cc	0.305	0.415
3 cc	7 cc	0.86	7 cc	3 cc	0.255	0.605
4 cc	6 cc	0.94	6 cc	4 cc	0.195	0.745
5 cc	5 cc	0.84	5 cc	5 cc	0.145	0.695
6 cc	4 cc	0.66	4 cc	4 cc	0.110	0.55
7 cc	3 cc	0.51	3 cc	3 cc	0.105	0.405
8 cc	2 cc	0.33	2 cc	2 cc	0.055	0.270
9 cc	1 cc	0.190	1 cc	1 cc	0.05	0.140

Fig. 2, Curve (3)

Table 6.

Set IV.

Concentration Vanadyl Sulphate = 2×10^{-4}M

Concentration of Ferron = 2×10^{-4}M

Wave length: 380 mu

Vol. of $VOSO_4$	Vol. of Ferron	O.D.	Vol. of Ferron	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.275	9 cc	1 cc	0.205	0.070
2 cc	8 cc	0.340	8 cc	2 cc	0.165	0.175
3 cc	7 cc	0.360	7 cc	3 cc	0.140	0.220
4 cc	6 cc	0.355	6 cc	4 cc	0.115	0.240
5 cc	5 cc	0.285	5 cc	5 cc	0.070	0.215
6 cc	4 cc	0.230	4 cc	6 cc	0.095	0.135
7 cc	3 cc	0.205	3 cc	7 cc	0.075	0.130
8 cc	2 cc	0.115	2 cc	8 cc	0.075	0.040
9 cc	1 cc	0.055	1 cc	9 cc	0.025	0.030

The results arrived at by Job's method of continuous variation were furthur confirmed by slope ratio method.[13] Two series of solutions were prepared by varying the concentration of one of the reagents in presence of constant amount of the other. Four sets of experiments were carried out.

Table 7.

Set I.

Vol. of $1x10^{-3}$M $VOSO_4$ = 0.5 cc

Strength of Ferron = $5x10^{-4}$M

After mixing, all the mixtures were diluted to 5 cc.

Set II.

Vol. of $1x10^{-3}$M Ferron = 0.5 cc

Strength of $VOSO_4$ = $5x10^{-4}$M

After mixing, all the mixtures were diluted to 5 cc.

Wave length 380 mu:

Set I		Set II	
Vol. of Ferron added	O.D.	Vol. of $VOSO_4$ added	O.D.
0 cc	-	0 cc	0.07
0.1 cc	-	0.1 cc	0.12
0.2 cc	0.055	0.2 cc	0.18
0.5 cc	0.115	0.5 cc	0.280
0.8 cc	0.205	0.8 cc	0.410
1.0 cc	0.350	1.0 cc	0.50
1.5 cc	0.50	1.5 cc	0.75
2.0 cc	0.58	2.0 cc	-
2.2 cc	0.64	2.2 cc	-
2.5 cc	0.64	2.5 cc	-
3.0 cc	0.67	3.0 cc	-
3.5 cc	0.75	3.5 cc	-
4.0 cc	0.70	4.0 cc	-

Fig. 3, Curve (1) Fig. 3, Curve (2)

Table 8.

Set III.

Vol. of $5x10^{-4}$M $VOSO_4$ = 0.5 cc

Strength of Ferron = $2x10^{-4}$M

After mixing of the reactants, all the solutions were diluted to 5 cc.

Set IV.

Vol. of $5x10^{-4}$ Ferron = 0.5 cc

Strength of $VOSO_4$ = $2x10^{-4}$M

After mixing the reactants, all the solutions were diluted to 5 cc.

Wave length: 380 mu

Set III		Set IV	
Vol. of $VOSO_4$ added	O.D.	Vol. of Ferron added	O.D.
0 cc	0.02	0	0.02
0.1 cc	0.03	0.1 cc	0.04
0.2 cc	0.035	0.2 cc	0.08
0.5 cc	0.075	0.5 cc	0.145
0.8 cc	0.115	0.8 cc	0.230
1.0 cc	0.135	1.0 cc	0.30
1.5 cc	0.20	1.5 cc	0.40
2.0 cc	0.270	2.0 cc	0.53
2.2 cc	0.30	2.2 cc	0.55
2.5 cc	0.34	2.5 cc	0.68
3.0 cc	0.39	3.0 cc	-
3.5 cc	-	3.5 cc	-
4.0 cc	-	4.0 cc	-

Fig. 3, Curve (3)

Fig. 3, Curve (3).

To study the influence of pH on the absorption of the complex, the mixtures of vanadyl sulphate ($2x10^{-5}M$) and Ferron ($2x10^{-5}M$) were prepared and their pH was adjusted (in the pH range 2.4 to 9.6) by adding buffer solutions. Absorption experiments were then carried out.

Table 9.

Concentration of $VOSO_4$ = $8x10^{-5}M$

Concentration of Ferron = $1.6x10^{-4}M$

Wave length (in mμ)	pH= 2.4 (1)	pH= 2.8 (2)	pH= 3.8 (3)	pH= 5.2 (4)	pH= 6.1 (5)	pH= 6.7 (6)	pH= 7.2 (7)	pH= 7.5 (8)	pH= 8.2 (9)	pH= 9.6 (10)
350	0.210	0.230	0.255	0.345	0.370	0.390	0.425	0.46	0.35	0.290
360	0.230	0.265	0.285	0.370	0.40	0.445	0.450	0.475	0.40	0.350
375	0.260	0.305	0.375	0.420	0.465	0.480	0.480	0.50	0.45	0.40
380	0.325	0.335	0.395	0.430	0.475	0.485	0.495	0.505	0.460	0.410
385	0.30	0.325	0.385	0.420	0.465	0.475	0.490	0.495	0.445	0.390
400	0.20	0.245	0.340	0.340	0.465	0.435	0.445	0.460	0.250	0.30
425	0.10	0.160	0.175	0.20	0.30	0.350	0.355	0.370	0.120	0.20
450	0.003	0.090	0.075	0.090	0.70	0.210	0.235	0.270	0.075	0.05
475	0.001	0.060	0.030	0.040	0.110	0.130	0.150	0.175	0.060	0.020
500	0.001	0.035	0.025	0.045	0.070	0.085	0.120	0.125	0.055	0.020
525	0.001	0.030	0.025	0.060	0.03	0.060	0.075	0.10	0.050	0.020
550	-	-	0.025	-	-	0.050	0.060	0.055	0.050	0.0250

Fig. 4, Curve (1),(2),(3),(4),(5),(6),(7),(8),(9) and (10).

The formation constant of the vanadyl ferron complex in solution was determined according to the method of Tanka and Takamura.[14]

If a, the total concentration of VO^{++} is in a large excess over b, the total concentration of Ferron, the concentration of the complex formed in solution, C, can be expressed by the equation.

$$C = \frac{K}{K(a-3c)(b-3c)} = \frac{Kab}{1-3aK}$$

Where K is the formation constant of the species in solution expressed in terms of molar concentration.

$$D = EC = \frac{E\,Kab}{(1-3aK)}$$

or $$\frac{ab}{D} = \frac{3a}{E} - \frac{1}{EK}$$

Where E is the molar extinction coefficent of the complex. By plotting $\frac{ab}{D}$ against a, a linear relationship is obtained, and from the values of the line and its intercept K and E can be determined (Fig. 5).

Conductometric studies on Vanadyl Sulphate-Ferron Complex:

Electrical conductance measurements were carried out with the help of Cambridge conductivity bridge and a dip type conductivity cell (K= 0.36).

Electrical conductance measurements were made with mixtures prepared according to Job's method of continuous variation. Equimolar solutions of the reagents of concentrations 1 x 10^{-3}M, 2 x 10^{-4}M and 5 x 10^{-4}M were prepared in conductivity water and conductances were measured at 30 ± 0.1°C. The difference is Sp conductivity observed Sp conductivity of the complex minus the sum of the conductivities of the constituent solutions was plotted against the composition of the mixture (Fig. 6).

Table 10.

Concentration of $VOSO_4$ = 1×10^{-3}M

Concentration of Ferron = 1×10^{-3}M

Vol. of $VOSO_4$	Vol. of Ferron	Conductivity of the Complex C	Vol. of $VOSO_4$	Vol. of H_2O	Conductivity of the mixture A	Vol. of Ferron	Vol. of H_2O	Conductivity of the mixture B	Sum of the conductivities A+B	Diff. in Conductances C-(A + B)
1 cc	9 cc	3.5×10^{-5}	1 cc	9 cc	1.51×10^{-5}	9 cc	1 cc	0.57×10^{-5}	2.08×10^{-5}	1.42×10^{-5}
2 cc	8 cc	4.1×10^{-5}	2 cc	8 cc	2.55×10^{-5}	8 cc	2 cc	1.24×10^{-5}	3.79×10^{-5}	0.30×10^{-5}
3 cc	7 cc	4.3×10^{-5}	3 cc	7 cc	1.66×10^{-5}	7 cc	3 cc	1.56×10^{-5}	3.22×10^{-5}	1.08×10^{-5}
4 cc	6 cc	4.2×10^{-5}	4 cc	6 cc	1.06×10^{-5}	6 cc	4 cc	1.57×10^{-5}	2.63×10^{-5}	1.57×10^{-5}
5 cc	5 cc	4.1×10^{-5}	5 cc	5 cc	1.24×10^{-5}	5 cc	5 cc	1.86×10^{-5}	3.0×10^{-5}	1.10×10^{-5}
6 cc	4 cc	3.45×10^{-5}	6 cc	4 cc	0.70×10^{-5}	4 cc	6 cc	2.15×10^{-5}	2.85×10^{-5}	0.60×10^{-5}
7 cc	3 cc	3.6×10^{-5}	7 cc	3 cc	0.98×10^{-5}	3 cc	7 cc	2.45×10^{-5}	3.43×10^{-5}	0.18×10^{-5}
8 cc	2 cc	2.55×10^{-5}	8 cc	2 cc	0.54×10^{-5}	2 cc	8 cc	1.70×10^{-5}	2.24×10^{-5}	0.31×10^{-5}
9 cc	1 cc	1.60×10^{-5}	9 cc	1 cc	0.59×10^{-5}	1 cc	9 cc	1.0×10^{-5}	1.59×10^{-5}	0.02×10^{-5}

Fig. 6, Curve 1.

Table 11.

Concentration of $VOSO_4$ = 5×10^{-4}M

Concentration of Ferron = 5×10^{-4}M

Vol. of $VOSO_4$	Vol. of Ferron	Conductivity of the Complex C	Vol. of $VOSO_4$	Vol. of H_2O	Conductivity of the mixture A	Vol. of Ferron	Vol. of H_2O	Conductivity of the mixture B	Sum of the conductivities (A + B)	Diff. in conductances C-(A + B)
1 cc	9 cc	5.3×10^{-4}	1 cc	9 cc	3.42×10^{-4}	9 cc	1 cc	1.83×10^{-4}	5.25×10^{-4}	0.05×10^{-4}
2 cc	8 cc	4.9×10^{-4}	2 cc	8 cc	2.95×10^{-4}	8 cc	2 cc	1.83×10^{-4}	4.78×10^{-4}	0.125×10^{-4}
3 cc	7 cc	4.4×10^{-4}	3 cc	7 cc	1.52×10^{-4}	7 cc	3 cc	2.70×10^{-4}	4.22×10^{-4}	0.180×10^{-4}
4 cc	6 cc	4.3×10^{-4}	4 cc	6 cc	1.90×10^{-4}	6 cc	4 cc	2.15×10^{-5}	4.05×10^{-4}	0.240×10^{-4}
5 cc	5 cc	3.8×10^{-4}	5 cc	5 cc	1.60×10^{-4}	5 cc	5 cc	2.0×10^{-4}	3.60×10^{-4}	0.20×10^{-4}
6 cc	4 cc	2.15×10^{-4}	6 cc	4 cc	1.41×10^{-4}	4 cc	6 cc	0.50×10^{-4}	1.91×10^{-4}	0.14×10^{-4}
7 cc	3 cc	1.82×10^{-4}	7 cc	3 cc	1.27×10^{-4}	3 cc	7 cc	0.58×10^{-4}	1.85×10^{-4}	0.07×10^{-4}
8 cc	2 cc	1.38×10^{-4}	8 cc	2 cc	0.68×10^{-4}	2 cc	8 cc	0.63×10^{-4}	1.31×10^{-4}	0.07×10^{-4}
9 cc	1 cc	0.84×10^{-4}	9 cc	1 cc	0.06×10^{-4}	1 cc	9 cc	0.72×10^{-4}	0.78×10^{-4}	0.06×10^{-4}

Fig. 6, Curve 2.

Fig. 3.

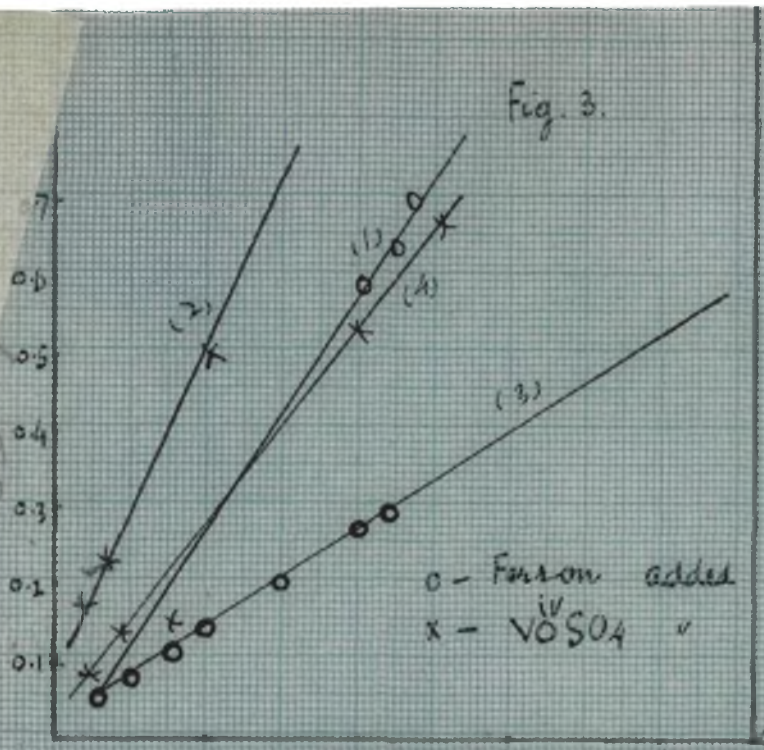


Fig. 5

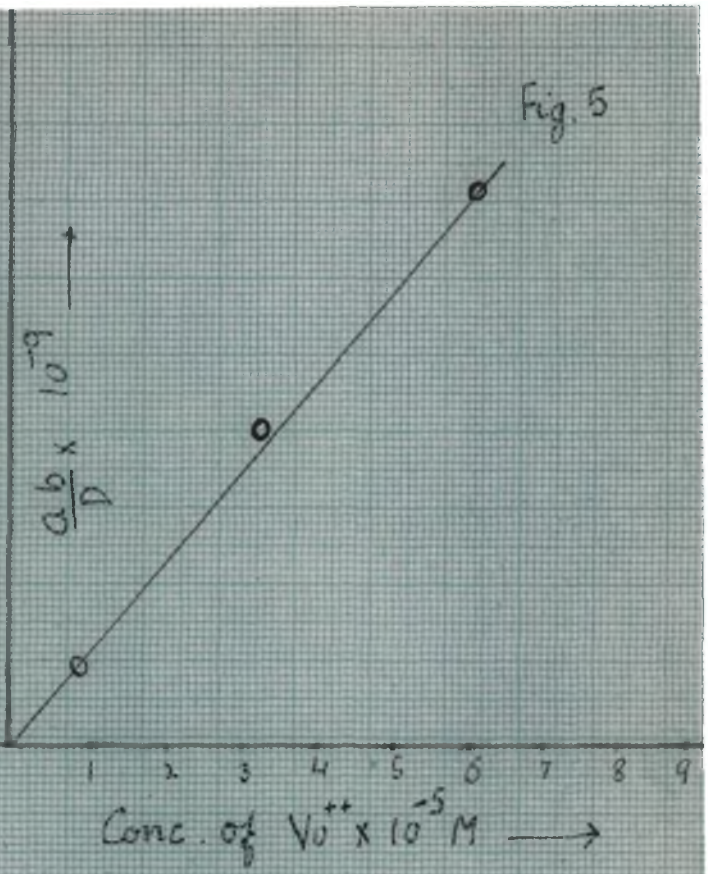


Fig. 6

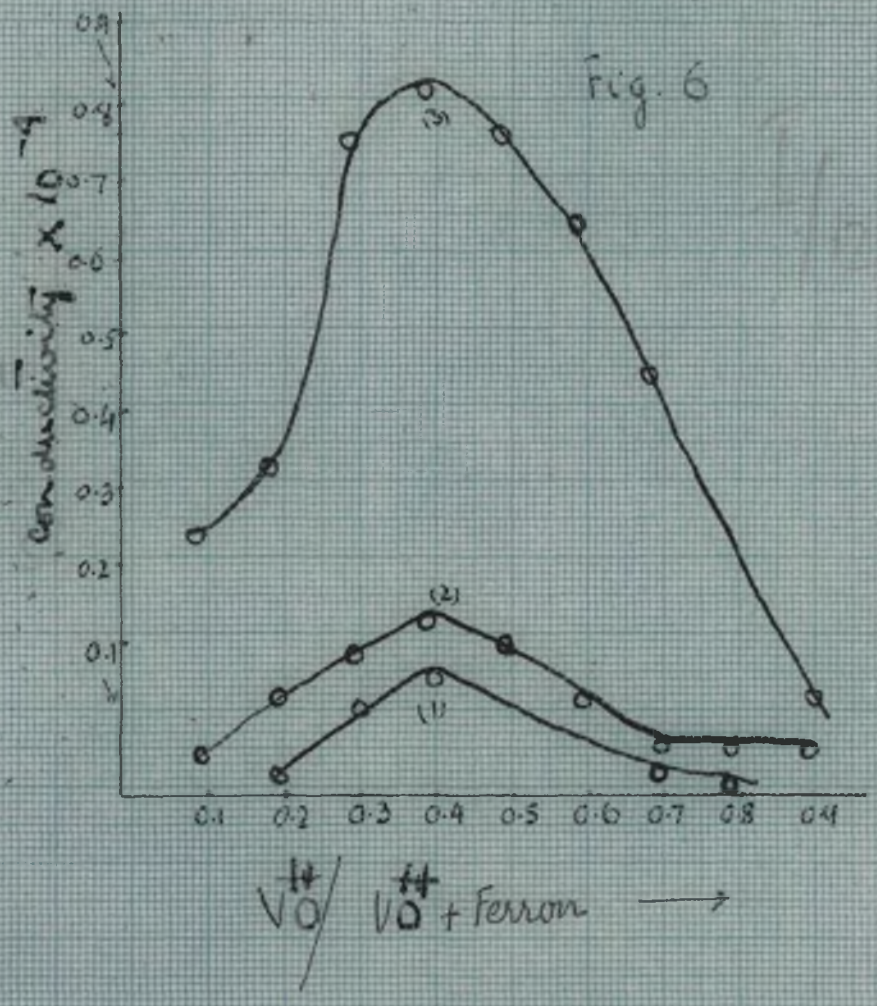


Table 12.

Concentration of $VOSO_4$ = 2×10^{-4}M

Concentration of Ferron = 2×10^{-4}M

Vol. of $VOSO_4$	Vol. of Ferron	Conductivity of the Complex C	Vol. of $VOSO_4$	Vol. of H_2O	Conductivity of the mixture A	Vol. of Ferron	Vol. of H_2O	Conductivity of the mixture B	Sum of the conductivities (A + B)	Diff. in conductance C-(A + B)
1 cc	9 cc	1.72×10^{-4}	1 cc	9 cc	1.2×10^{-4}	9 cc	1 cc	0.184×10^{-4}	1.384×10^{-4}	0.336×10^{-4}
2 cc	8 cc	1.86×10^{-4}	2 cc	8 cc	0.90×10^{-4}	8 cc	2 cc	0.540×10^{-4}	1.44×10^{-4}	0.42×10^{-4}
3 cc	7 cc	2.1×10^{-4}	3 cc	7 cc	0.66×10^{-4}	7 cc	3 cc	0.58×10^{-4}	1.24×10^{-4}	0.86×10^{-4}
4 cc	6 cc	2.3×10^{-4}	4 cc	6 cc	0.74×10^{-4}	6 cc	4 cc	0.65×10^{-4}	1.39×10^{-4}	0.91×10^{-4}
5 cc	5 cc	1.78×10^{-4}	5 cc	5 cc	0.48×10^{-4}	5 cc	5 cc	0.45×10^{-4}	0.93×10^{-4}	0.85×10^{-4}
6 cc	4 cc	1.70×10^{-4}	6 cc	4 cc	0.57×10^{-4}	4 cc	6 cc	0.39×10^{-4}	0.969×10^{-4}	0.74×10^{-4}
7 cc	3 cc	1.98×10^{-4}	7 cc	3 cc	0.48×10^{-4}	3 cc	7 cc	1.04×10^{-4}	1.52×10^{-4}	0.54×10^{-4}
8 cc	2 cc	1.70×10^{-4}	8 cc	2 cc	0.29×10^{-4}	2 cc	8 cc	1.06×10^{-4}	1.35×10^{-4}	0.35×10^{-4}
9 cc	1 cc	1.56×10^{-4}	9 cc	1 cc	0.20×10^{-4}	1 cc	9 cc	1.35×10^{-4}	1.55×10^{-4}	0.11×10^{-4}

Fig. 6, Curve 3.

D I S C U S S I O N

The spectrophotometric methods carried out to study the Vanadyl sulphate - Ferron complex gave the following information regarding the composition of the complex.

(i) The method of Vosburgh and Cooper employed to determine the number of complexes formed showed that all the mixtures gave a maxima at 380 mu, thereby showing the formation of only one complex (Fig. 1, Table 1) and the λ_{max} of the ferron lies at 380 mu (Fig. 1, Table 2).

(ii) Job's method of continuous variation carried out for the equimolar solutions of $VOSO_4$ and Ferron of four different concentrations viz., 1×10^{-3}M, 2×10^{-4}M, 4×10^{-4}M and 8×10^{-4}M gave a ratio 2:3 for VO^{++} and Ferron (Fig. 2, Table 3, 4, 5 and 6).

(iii) The results arrived at by the Job's method were further conformed by the slope ratio method. The concentration of $VOSO_4$ (1×10^{-4}M) was kept constant and that of Ferron of concentration 5×10^{-4}M was varied in the first set, while in the other, the concentration of Ferron (1×10^{-4}) was kept constant that of $VOSO_4$ (5×10^{-4}M) was varied (Table 7, Fig. 3). Two more sets were prepared by taking different concentrations of $VOSO_4$ and Ferron and O.D. were measured (Table 8, Fig. 3). The slope was

determined on the straight line portion of the curve and a ratio of 2:3 for Set I, II and III, IV was obtained.

The value of formation constant was calculated from the expression given on page 123 of this chapter.

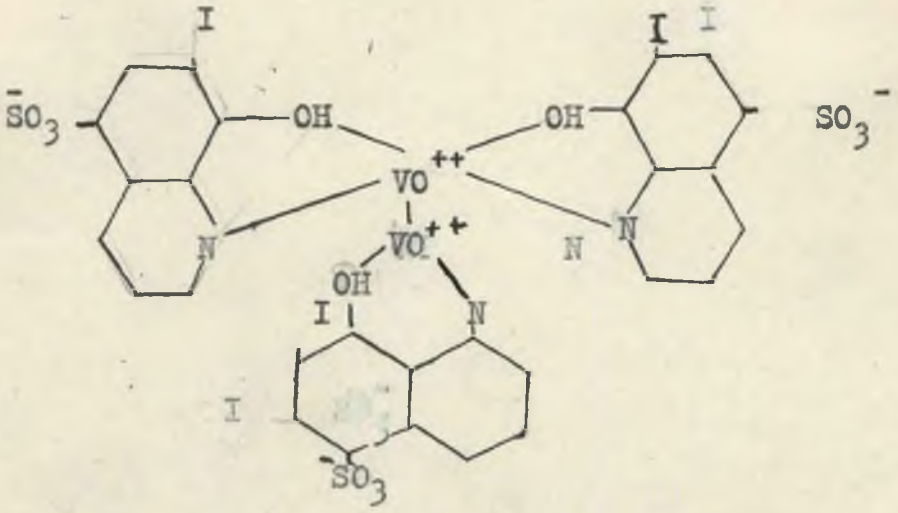
O.D. measurements for VO^{++} Ferron mixtures were made by varying the concentration of VO^{++} and Ferron from 4.8×10^{-4}M up to 1.6×10^{-5}M in presence of a fixed higher concentration of VO^{++} and Ferron (1×10^{-4}M) respectively (Fig. 3, Curve 1, 2). Another set of experiments was carried out by varying the concentration of VO^{++} from 4×10^{-6} to 1.2×10^{-4}M in presence of a law fixed concentration of Ferron (5×10^{-5}M) and measuring the absorbances of the solutions at 380 mu (Fig. 3, curve 4). The results are given in the Table 13 and the values of a b/D are plotted against the concentration of VO^{++} (a) in fig. 6.

Table 13.

Conc. of VO^{++} a x 10^{-5}	D (observed)	$ab/_D \times 10^{-9}$
0.8	0.07	5.71
3.12	0.24	6.5
4.0	0.28	7.1
6.0	0.41	7.29
8.0	0.55	7.21

Fig. 6.

studies, the structure of the complex may be written as



The utility of the vanadyl sulphate - Ferron reaction can be found in the colorimetric estimation of VO^{++} ions. Since the colour of the complex remains stable over a large pH range (approximately 2 to 11) and the intensity of the colour does not fade upto as low a concentration as 10^{-4}M, the reagent can be very well employed for the estimation of vanadyl ions.

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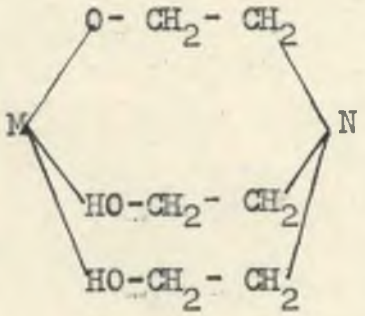
C H A P T E R IV.

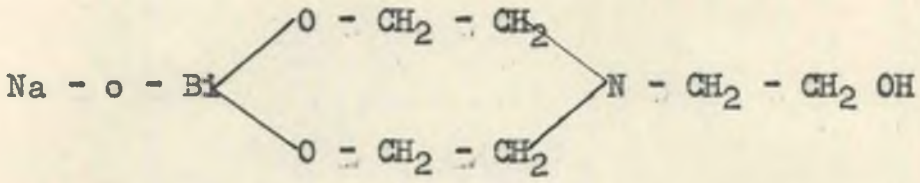
Ethanol Amine Complexes of V(iv)

ETHANOL AMINES COMPLEXES OF V(iv)

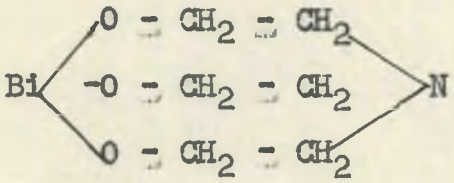
The strong complex forming tendency of ethanolamines are well known, the coordination takes place usually through oxygen or nitrogen depending upon the nature of the metal ion. Ethanol amines form complexes with almost all the metals of the transitional series, the most extensively studied are those of Fe, Co, Ni, Cu and Mn.[1,2,3] Tettamanzi and Carli[4] made an extensive study of the ethanolamine complexes of Ni, Cd, Ca, Mg. They suggested that in nickel complexes the coordination takes place through -OH group, whereas magnesium formed simple addition compounds. Furthur work by the same authors[5] showed that in Co, Cu or Zn complexes, a hydrogen of one of the hydroxyl groups was replaced by the metal giving a compound which they formulated.



Miller[6] has prepared some crystalline derivatives of bismuth wi triethanolamine and from analytical data, be assigned the formula.



and



Some fresh light was also shed on the nature of ethanolamine complexes by employing polarographic studies R.S. Subramayan[7] showed that ethanol amines give reversible wave only in ammonical solutions while in non ammonical solutions reversible wave is obtained only with triethanol-amine. He also studied the polarographic behaviour of Cd, Cu, Pb, Ni, Co, Zn and Fe in ethanol amines using $K_2 SO_4$ as supporting electrolyte. He showed the formation of complexes like Cd (Mono en)$_3^{++}$, Cd (Dien)$_3^{++}$, Cd (Trien)$^{++}$, Ni (Dien)$^{++}$ Ni (Monoen)$_3^{++}$, Pb (Dien)$_2^{++}$, Pb (Monoen)$_2^{++}$ etc. Michelle Gilband[8] studied the effect of pH on the complexing action of triethanol amine on copper salts. Triethanol amine give active complexes with copper salts having molecular or the particularly ionised form depending on pH. Neutral or alkali media favours mobility of the hydroge on alcoholic OH. He determined condensation domain of existence and stability constant of the different complexes

by employing potentiometric, cryoscopic and polarographic measurements. The dissociation constants for the complex Cu(ii)-triethanolamine, $T_2Cu_2(OH)_2^{2+}$ $T_4Cu_4(OH)_5^{3+}$ and $T_2Cu_2(OH)_4$ are given by pK= 4.7, 27.9, 63.5 and 40.0 respectively and for $T + Cu(OH)_4^{2-} \rightleftharpoons TCu(OH)_4^{2-}$ as 3.4.

A review of the existing literature shows that ethanol amine complexes of almost all the transitional metals belonging to first long period have been studied except that of vanadium. Hence, an attempt was made to study the vanadyl complexes of ethanol amines by applying physico-chemical methods. In this chapter the results on the composition of the products of V(iv)-ethanol amine complexes employing spectrophotometric and amperometric methods, are described.

EXPERIMENTAL

SOLUTIONS:

Monoethanolamine solution (approx 1M) was prepared by 12.0 cc of the reagent (Extra pure, Naarden product) in 10.0 cc doubly distilled water and was standardized by titrating against 1M HCl pH metrically. Diethanol amine (E. Merck) and Triethanol amine (Naarden) were employed

for the experiments and their approximately molar solutions were prepared by dissolving 9.6 cc and 6 cc respectively in 100 cc of doubly distilled water. They were standardized pH meterically against 1M HCl. The pH metric titrations were carried out with a Beckman pH meter (moldel C) with glass electrodes of general utility.

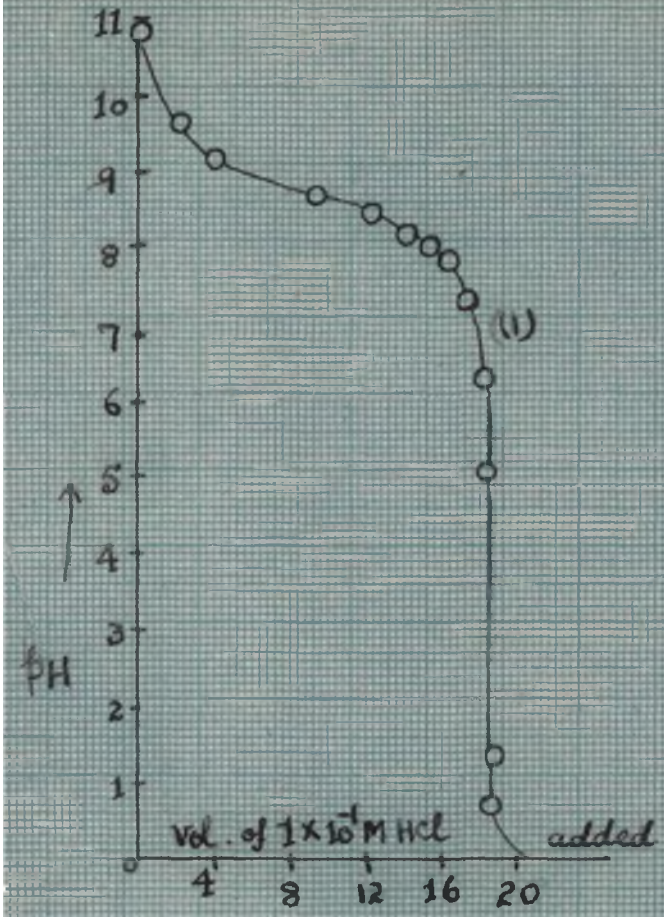
Table I

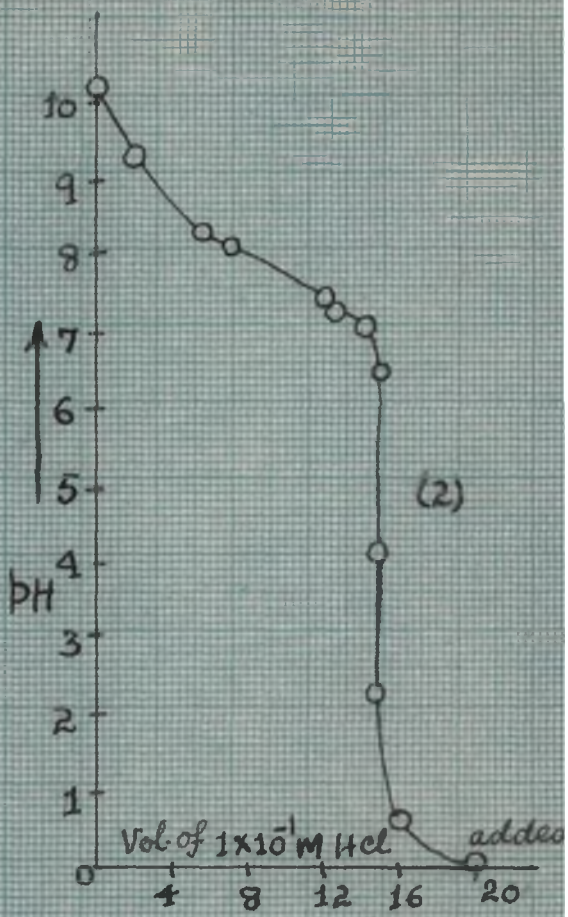
Set I. 15 cc $\frac{M}{10}$ monoethanolamine (approximate $M/_{10}$ solution was 10 cc of approximate M solution of monoethanolamine to 100 cc) against standard $\frac{M}{10}$ HCl.

Set II. 15 cc $\frac{M}{10}$ Diethanolamine (approximate $\frac{M}{10}$ solution was prepared by diluting 10 cc of approximate M solution of the reagent to 100 cc) against standard $\frac{M}{10}$ HCl.

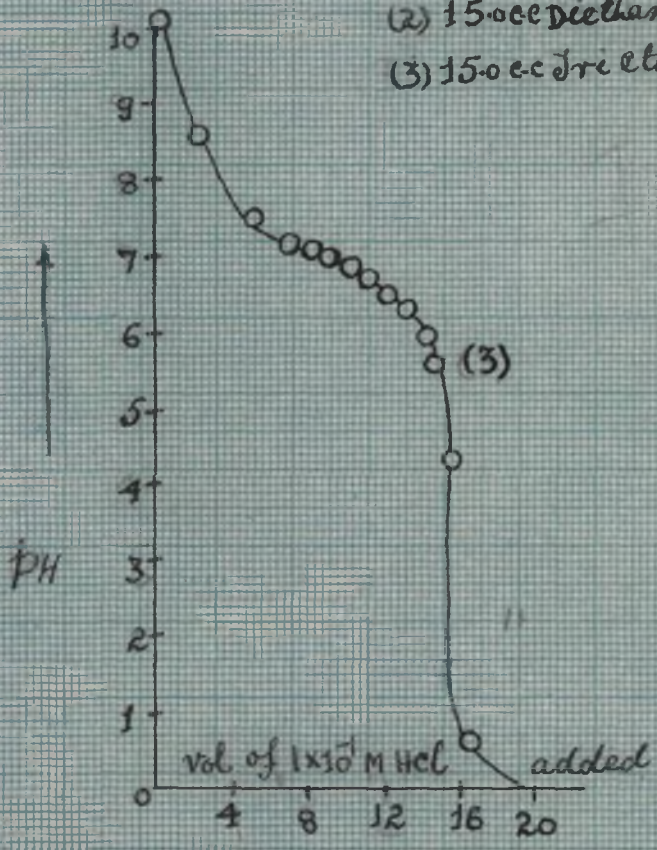
Set III. 15 cc $\frac{M}{10}$ Triethanolamine (approximate $\frac{M}{10}$ solution was prepared by diluting 10 cc of approximate M solution of the reagent to 100 cc) against standard $\frac{M}{10}$ HCl.

Fig 1





(1) 15.0 cc Monoethanol amine
(2) 15.0 cc Diethanol amine
(3) 15.0 c.c Triethanol amine



Vol. of $\frac{M}{10}$ HCl added	pH (1)	pH (2)	pH (3)
0	10.7	10.1	10.0
2 cc	9.5	9.2	8.5
4 cc	9.1	8.6	7.6
5 cc	9.0	8.2	7.4
7 cc	8.8	8.0	7.1
8 cc	8.7	7.9	7.0
9 cc	8.6	7.8	6.9
10 cc	8.5	7.7	6.8
11 cc	8.5	7.6	6.6
12 cc	8.4	7.4	6.4
14 cc	8.1	7.0	5.9
15 cc	8.0	6.4	4.3
16 cc	7.8	0.6	0.6
18 cc	6.5	0.2	-
18.5cc	1.3	-	-

Fig. (1)

i) 17.5 cc MCl ($1x10^{-1}$M)$\equiv$ 15.0 cc Mono ethanolamine

ii) 13.5 cc MCl ($1x10^{-1}$M)$\equiv$ 15.0 cc Diethanolamine

iii) 15.0 cc MCl ($1x10^{-1}$M)$\equiv$ 15.0 cc Triethanolamine

An approximate $1x10^{-1}$M solution of vanadyl chloride was prepared by dissolving the reagent (E. Merck) in double distilled water and its strength was determined by reducing its on Jone's reductor and titrating it against $KMnO_4$ solution (details given in chapter I page 24).

Buffer solution of the pH range (2 to 11) were prepared by utilising universal buffer containing mixture of ph Acetic acid boric acid, phosphoric acid and sodium hydroxide (All A.R. Products). The pH's of the buffer solutions and mixtures were checked with a Beckman pH meter (modle G) with glass electrodes (general utility and E type electrode for pH's above 10). A Beckman D.U. Spectrophotometer with tungston lamp as the light source was used for optical density measurements. The amperometric measurements were made using the Fischer Elecdropode in conjunction with a multiflex galvanometer type MGF_2 in the external circuit.

V(iv)- MONO ETHANOL AMINE COMPLEX:

Vanadyl chloride formed a soluble yellowish green coloured complex with mono ethanol amine, the colour of the complex faded on long exposure to air, however, on keeping a layer of paraffin on the surface, it remained stable for several days. Hence, during the experiments the mixture of the reactants were kept covered with a thin layer of liquid paraffin in order to check the fading.

In order to determine the number of complexes formed by the interaction of vanadyl chloride and monoethanol amine the method of Vosburgh and Cooper[9] was followed. Equimolar

solution ($1x10^{-2}M$) of vanadyl chloride and mono ethanol amine were mixed in the ratio of 2:8, 3:7, 4:6, 5:5 and 6:4 respectively and the absorbances were measured in the wave length range 400 to 1000 mu.

Table 2.

Concentration of vanadyl chloride = $1x10^{-2}M$

Concentration of Monoethanolamine = $1x10^{-2}M$

Wave length mu	2:8 (1)	3:7 (2)	4:6 (3)	5:5 (4)	6:4 (5)
400	0.185	0.325	0.570	0.68	0.70
425	0.120	0.270	0.440	0.58	0.480
450	0.125	0.230	0.355	0.410	0.30
475	0.110	0.210	0.315	0.280	0.150
500	0.10	0.20	0.30	0.220	0.040
525	0.090	0.190	0.30	0.210	0.020
550	0.085	0.190	0.305	0.205	0.010
575	0.090	0.195	0.305	0.230	0.020
600	0.075	0.20	0.320	0.235	0.060
625	0.090	0.205	0.350	0.280	0.110
650	0.120	0.30	0.390	0.330	0.160
675	0.075	0.250	0.380	0.30	0.120
700	0.070	0.225	0.360	0.280	0.10
725	0.070	0.245	0.350	0.270	0.110
750	0.070	0.240	0.340	0.280	0.110
800	0.070	0.255	0.340	0.280	0.120
850	0.080	0.270	0.330	0.285	0.120
900	0.070	0.280	0.335	0.290	0.130
950	0.060	0.280	0.330	0.285	0.140
1000	0.060	0.30	0.330	0.30	0.135

Fig. 2.

Job's method[7] was followed for determining the composition of the complex. Equimolar solutions of vanadyl chloride and mono ethanolamine of three different concentrations viz., $2x10^{-2}M$, $1x10^{-2}M$ and $5x10^{-3}M$ were mixed according to the method of continuous variation and O.D. was measured at 650 mu. The absorption of wolution containing the reactants seperately was also measured. Vanadyl chloride showed little absorption at this wave length but there was negligible absorption in case of mono ethanolamine. The difference in optical density was plotted against the ratio $\frac{VO^{++}}{VO^{++} + M.E.}$

Table 3.

Concentration of vanadyl chloride = $2x10^{-2}M$

Concentration of Mono ethanolamine= $2x10^{-2}M$

Wave length: 650 mu

Vol. of vanadyl chloride	Vol. of Mono ethanol amine	O.D.	Vol. of vanadyl chloride	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.095	1 cc	9 cc	0.040	0.040
2 cc	8 cc	0.195	2 cc	8 cc	0.055	0.140
3 cc	7 cc	0.480	3 cc	7 cc	0.80	0.40
4 cc	6 cc	0.795	4 cc	6 cc	0.095	0.70
5 cc	5 cc	0.715	5 cc	5 cc	0.125	0.590
6 cc	4 cc	0.540	6 cc	4 cc	0.140	0.40
7 cc	3 cc	0.435	7 cc	3 cc	0.165	0.270
8 cc	2 cc	0.360	8 cc	2 cc	0.180	0.180
9 cc	1 cc	0.214	9 cc	1 cc	0.210	0.03

Fig. 3, Curve (1).

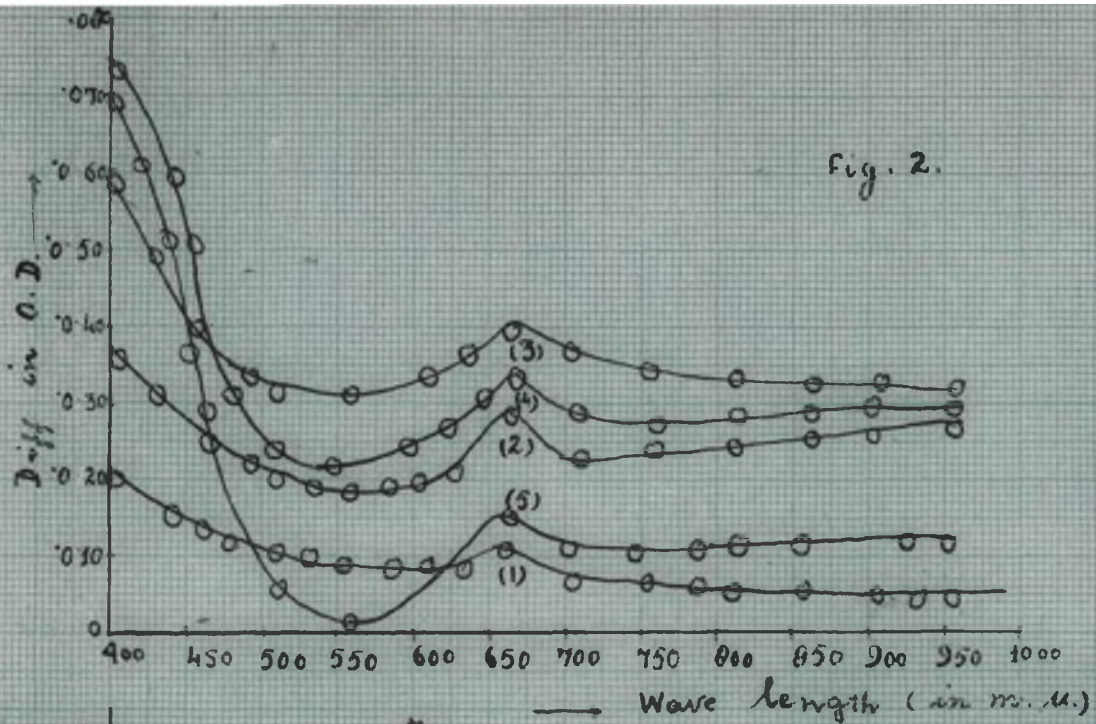


Fig. 2.

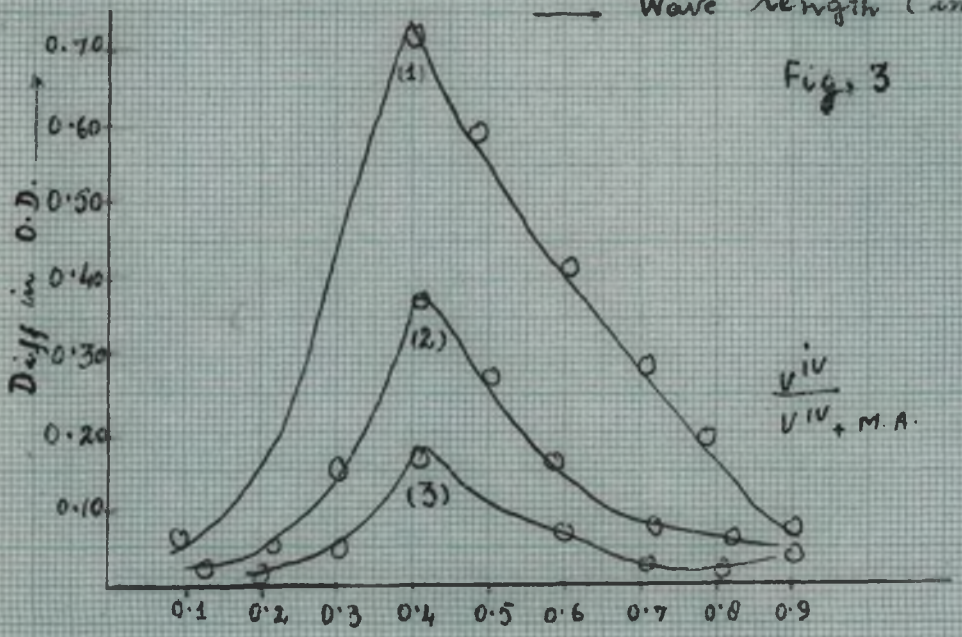
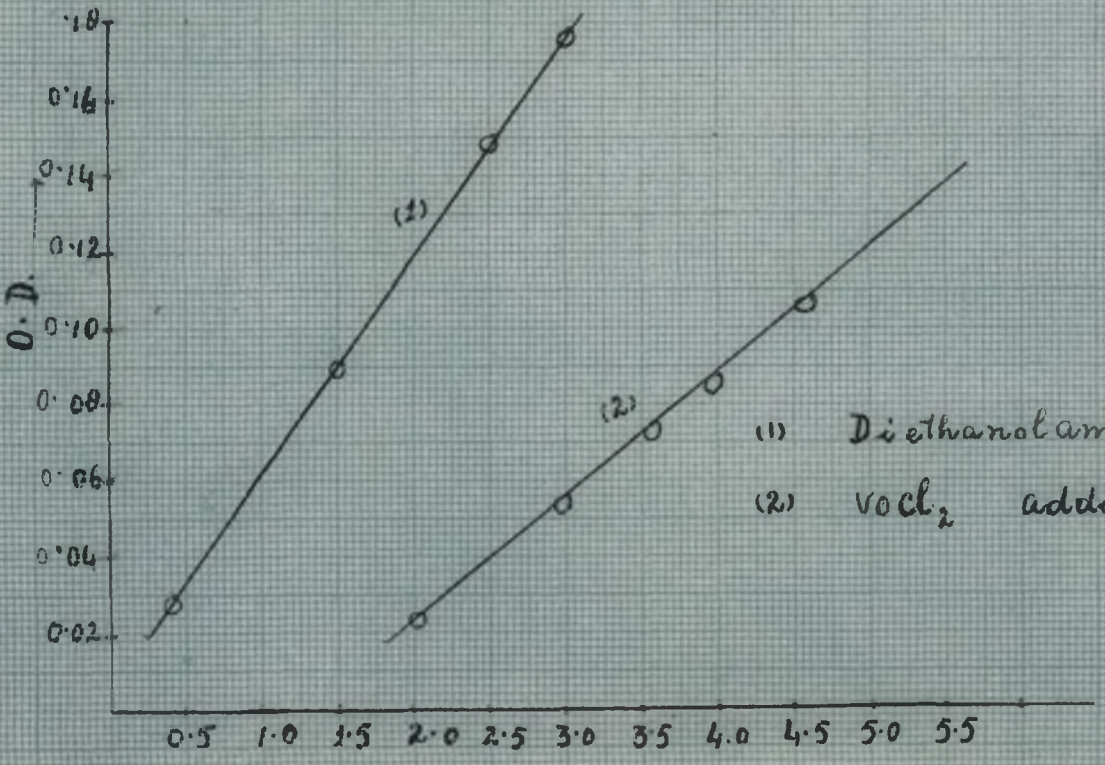


Fig. 3



(1) Diethanolamine added

(2) $VOCl_2$ added.

Table 4.

Concentration of Vanadyl chloride = 1×10^{-2}M

Concentration of Mono ethanolamine = 1×10^{-2}M

Wave length : 650 mu

Vol. of Vanadyl chloride	Vol. of monoethanol amine	O.D.	Vol. of Vanadyl chloride	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.020	1 cc	9 cc	0.020	0
2 cc	8 cc	0.040	2 cc	8 cc	0.025	0.015
3 cc	7 cc	0.170	3 cc	7 cc	0.045	0.125
4 cc	6 cc	0.370	4 cc	6 cc	0.025	0.345
5 cc	5 cc	0.310	5 cc	5 cc	0.030	0.280
6 cc	4 cc	0.155	6 cc	4 cc	0.040	0.115
7 cc	3 cc	0.095	7 cc	3 cc	0.050	0.045
8 cc	2 cc	0.110	8 cc	2 cc	0.060	0.050
9 cc	1 cc	0.090	9 cc	1 cc	0.065	0.025

Fig. 3, Curve 2.

Table 5.

Concentration of Vanadyl Chloride = 5×10^{-3}M

Concentration of Monoethanolamine = 5×10^{-3}M

Wave length : 650 mu

Vol. of Vanadyl chloride	Vol. of Monoethanol amine	O.D.	Vol. of Vanadyl chloride	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0	1 cc	9 cc	0	0
2 cc	8 cc	0.01	2 cc	8 cc	0	0.010
3 cc	7 cc	0.050	3 cc	7 cc	0.005	0.045
4 cc	6 cc	0.155	4 cc	6 cc	0.005	0.150
5 cc	5 cc	0.110	5 cc	5 cc	0.010	0.10
6 cc	4 cc	0.07	6 cc	4 cc	0.02	0.050
7 cc	3 cc	0.02	7 cc	3 cc	-	0.020
8 cc	2 cc	0.02	8 cc	2 cc	0.010	0.010
9 cc	1 cc	0.03	9 cc	1 cc	0.010	0.020

Fig. 3, Curve 3.

In order to get conclusive information regarding the composition of the complex, the method of slope ratio[8] was also conducted. Two sets of experiment were carried out. In the first set the concentration of vanadyl chloride was kept constant and that of monoethanolamine was varied, in other set the mixing was done in reverse order.

Table 6.

Set I.

Vol. of 2×10^{-2}M vanadyl chloride = 0.2 cc

Strength of monoethanolamine = 5×10^{-3}M

Set II.

Vol. of 2×10^{-2}M Monoethanolamine = 0.2 cc

Strength of vanadyl chloride = 5×10^{-3}M

After mixing all the solutions (Set I and Set II) were diluted to 5 cc and their O.D. was measured at 650 mu.

Set I.

Vol. of monoethanol amine added	O.D.	Vol. of vanadyl chloride added	O.D.
0	0.008	0	-
0.2	0.016	0.2	-
0.4	0.030	0.4	-
0.6	0.040	0.6	-
0.8	0.052	0.8	-
1.0	0.060	1.0	0.015
1.5	0.092	1.5	0.020
2.0	0.12	2.0	0.025
2.5	0.15	2.5	0.040
3.0	0.18	3.0	0.055
		4.0	0.085
		4.5	1.10
		4.8	1.20

Fig. 4, Curve 1 Fig. 4, Curve 2.

In order to study the influence of pH on the absorption of the complex, equimilar mixtures of vanadyl chloride and monoethanolamine of concentration 5×10^{-3}M were mixed in the ratio of 2:3 and their pH was adjusted to the required value by adding buffer solutions. Absorbance of all these mixtures were measured in the wavelength range of 400 mu to 1000 mu.

Table 7.

Concentration of vanadyl chloride = 5×10^{-3}M
Concentration of Monoethanolamine = 5×10^{-3}M

Wave length : 650 mu

Wave length mu	pH = 4.9 (1)	pH = 4.9 (2)	pH = 5.5 (3)	pH = 6.6 (4)	pH = 6.9 (5)	pH = 7.4 (6)	pH = 8.3 (7)	pH = 9.0 (8)	pH = 10.9 (9)	pH = 11.4 (10)
400	0.490	0.750	0.80	0.190	0.30	0.160	0.120	0.235	0.350	0.285
425	0.345	0.540	0.60	0.130	0.250	0.110	0.070	0.20	0.30	0.20
450	0.255	0.420	0.49	0.110	0.20	0.08	0.060	0.165	0.210	0.10
500	0.195	0.330	0.395	0.110	0.140	0.07	0.060	0.110	0.070	0.02
550	0.215	0.355	0.380	0.105	0.160	0.09	0.050	0.120	-	0.03
575	0.240	0.390	0.395	0.10	0.180	0.070	0.060	0.130	-	0.035
600	0.270	0.420	0.430	0.085	0.190	0.070	0.040	0.140	0.02	0.020
625	0.285	0.440	0.470	0.080	0.220	0.070	0.070	0.160	0.04	0.020
650	0.295	0.460	0.490	0.140	0.250	0.095	0.115	0.180	0.07	0.030
700	0.360	0.580	0.550	0.10	0.170	0.060	0.020	0.120	0.01	-
750	0.390	0.590	0.590	0.080	0.150	0.075	0.030	0.115	-	-
800	0.40	0.60	0.60	0.110	0.20	0.080	0.050	0.140	-	-
850	-	0.60	0.60	0.090	0.15	0.070	0.040	0.120	0.01	-
900	0.410	0.60	0.61	0.090	0.15	0.070	0.050	0.110	-	-
950	-	0.60	0.61	0.070	0.15	0.075	0.050	0.10	0.01	-
1000	-	0.60	0.61	0.070	0.14	0.075	0.050	0.10	0.01	-

Fig. 5.

The formation constant of the Vanadyl-Mono-ethanolamine complex in solution was determined according to the method of Tanaka and Takamura. The details of the method and required equations are given in Chapter III page 123.

Optical density measurements for VO^{++} ± Monoethanolamine mixtures were made by varying the concentration of VO^{++} and monoethanolamine upto 2.5×10^{-3}M in presence of higher concentration of VO^{++} Monoethanolamine (8×10^{-3}M) respectively showed that Beer' law is obyed under these conditions. Another set of experiments was carried out by varying the concentration of VO^{++} from 1×10^{-3}M to 4.8×10^{-3}M in presence of a low fixed concentration of Monoethanolamine (8×10^{-4}M) (Fig. 4, Curve 2) The results are given in table 8 and the values of $ab/_D$ are plotted against the concentration of VO^{++} in Fig. 6.

Table 8.

Conc. of VO^{++} ($x10^{-3}_a$M)	D observed	$ab/_D x10^{-5}$
1.0	0.015	5.50×10^{-5}
1.5	0.020	6.0×10^{-5}
2.0	0.025	6.40×10^{-5}
2.5	0.040	5.0×10^{-5}
3.0	0.055	4.33×10^{-5}
4.0	0.085	3.76×10^{-5}
4.5	1.10	3.27×10^{-5}
4.8	1.20	3.20×10^{-5}

Fig. 6a

Amperometric Titrations:

Amperometric titrations between vanadyl chloride and mono ethanol amine were carried out using sulphuric acid as supporting electrolyte and gelatin as maximum suppressor. The concentration of sulphuric acid was kept 6.6×10^{-2}M and that of gelatin 6.6×10^{-3}M. Both direct (vanadyl chloride in the cell) and reverse (monoethanolamine in the cell) titrations were carried out with different concentrations of the reactants. However, the reverse titrations did not prove successful as no sharp points of inflexion were obtained in these cases.

Direct:

1. 5.0 cc of 5×10^{-2}M vanadyl chloride + 10 cc H_2SO_4 (2×10^{-1}M) + 2 cc gelatin (1×10^{-1}%) + 13 cc H_2O against 2×10^{-1}M monoethanolamine.

2. 10.0 cc of 5×10^{-2}M vanadyl chloride + 10 cc H_2SO_4 (2×10^{-1}M) + 2 cc gelatin (1×10^{-1}%) + 8 cc H_2O against 2×10^{-1}M monoethanolamine.

3. 15 cc of 5×10^{-2}M vanadyl chloride + 10 cc H_2SO_4 (2×10^{-1}M) + 2 cc gelatin (1×10^{-1}%) + 3 cc H_2O against 2×10^{-1}M monoethanolamine.

Fig 6a

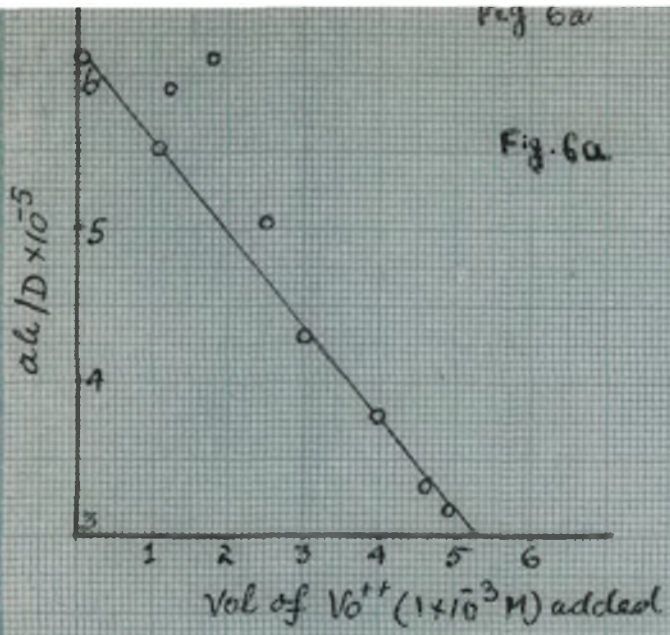


Fig 7

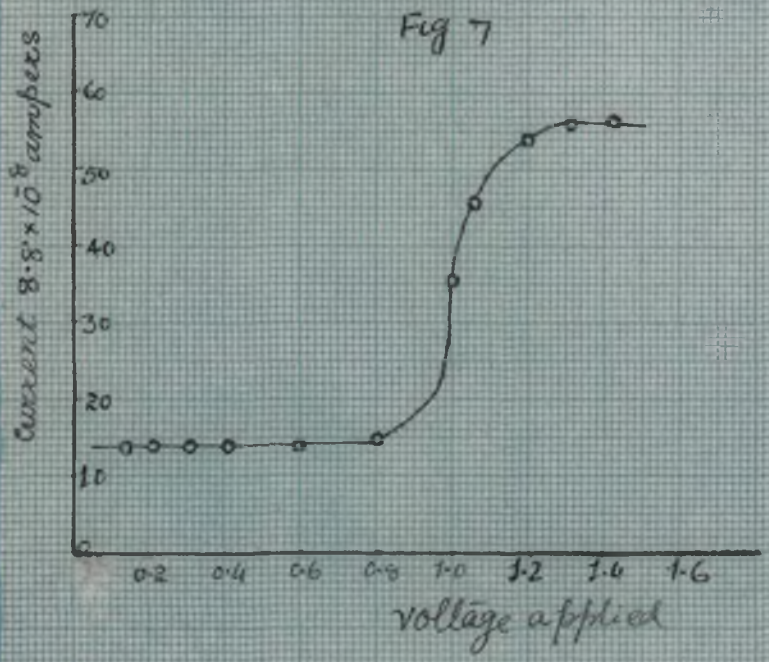
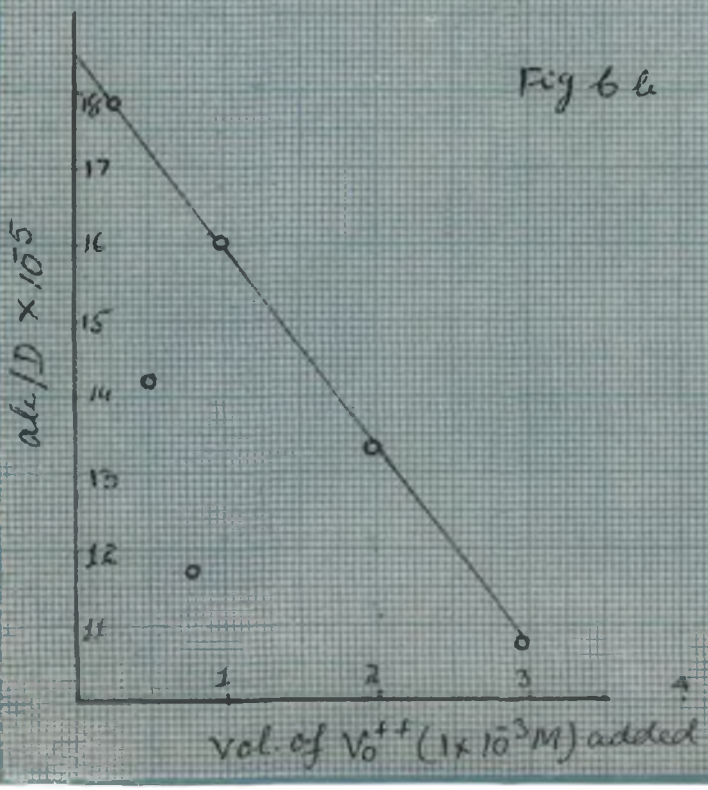


Fig 6 b



In order to carry out amperometric titrations the constant potential to be applied during the course of titrations was first of all determined 1.0 cc of $1x10^{-2}M$ vanadyl chloride in $8x10^{-2}M$ H_2SO_4 as supporting electrolyte was taken in the polarographic cell, the total voloume was made upto 25 cc. The current was measured at 1: 10 sensitivit of the galvanometer and 5 x sensitivity of the elecdropode. Nitrogen gas (purified after passing through alkaline pyragallol and chromus chloride) was passed for keeping an inert atmosphere. The cell was kept immersed in a thermostat maintained at 30± 0.1°c. The drop time was kept at 3.5 sec.

Table 9.

Polarogram of vanadyl chloride in sulphuric acid($8x10^{-2}M$)

Concentration of vanadyl chloride = $4x10^{-4}M$

Voltage applied	Current $8.8x10^{-8}$ amp.	Voltage applied	Current $8.8x10^{-8}$ amp.
0	13.50	1.25	55.5
0.10	14.0	1.30	56.0
0.15	14.0	1.35	56.5
0.20	14.0	1.40	57.0
0.30	14.0	1.45	57.0
0.40	14.5	1.50	57.0
0.50	14.5		
0.60	14.5		
0.70	15.0		
0.80	15.0		
0.85	16.5		
0.90	18.0		
0.95	19.0		
1.0	35.0		
1.05	46.5		
1.10	50.0		
1.15	52.5		
1.20	54.0		

Fig. 7.

Fig. 5

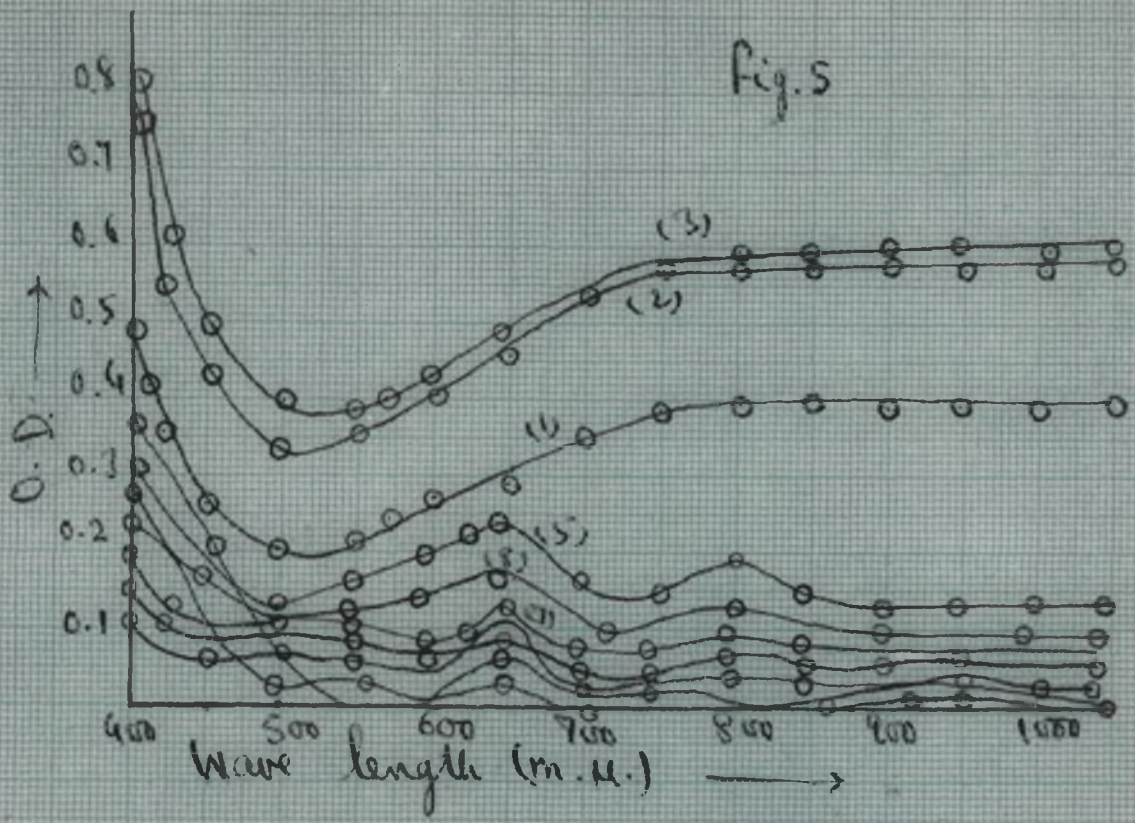
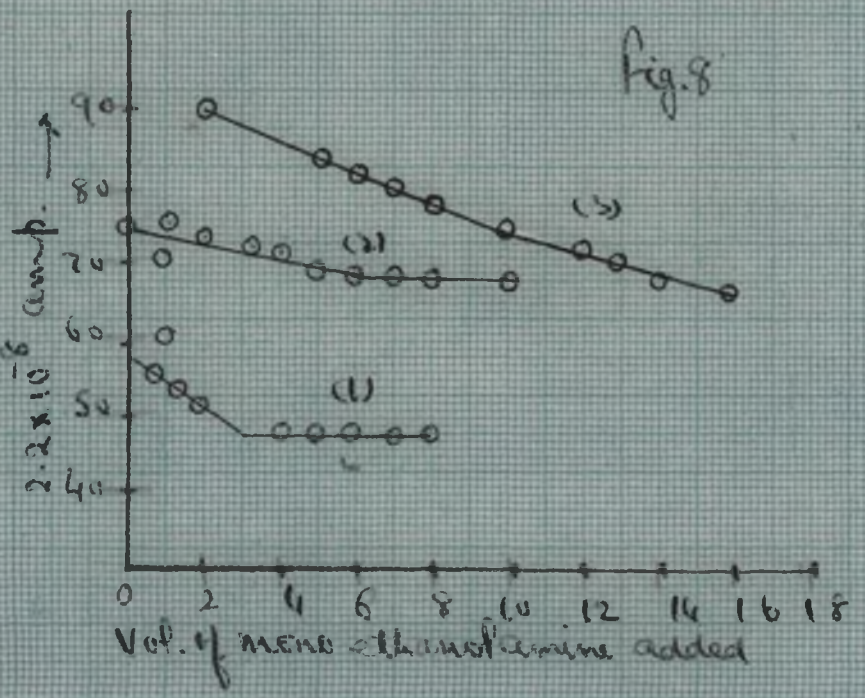

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
O.D.
(3)
(2)
(1)
(5)
(4)
400
500
600
700
800
900
1000
Wave length (m.μ.)

Fig. 8


90
80
70
60
50
40
2·2×10⁻⁶ amp.
(3)
(2)
(1)
0
2
4
6
8
10
12
14
16
18
Vol. of mono ethanolamine added

Polarogram was drawn and from the plateau of the curve, the potential to be applied for the amperometer titrations was determined and it came out to be -1.0 volt.

Direct titrations: vanadyl chloride in the cell

Table 10.

30 cc of 8.3×10^{-3}M vanadyl chloride against 2×10^{-1}M monoethanolamine.

Vol. of monoethanolamine	Current amp. (2.2×10^{-8})	Vol. of monoethanolamine	Current amp. (2.2×10^{-8})
0.0 cc	58.5	3.5	48.25
0.5 cc	56.0	4.0	47.25
1.0 cc	53.0	4.5	48.0
1.5 cc	52.5	5.0	48.0
2.0 cc	50.5	5.5	46.5
2.5 cc	49.5	6.0	48.0
3.0 cc	48.0		

Fig. 8, Curve 1.

Table 11.

30 cc of 1.66×10^{-2}M vanadyl chloride against 2×10^{-1}M monoethanolamine.

Vol. of monoethanolamine	Current amp. (2.2×10^{-8}	Vol. of monoethanolamine	Current amp. (2.2×10^{-8}
0 cc	74.5	8.0 cc	68.0
1.0 cc	75.0	9.0 cc	68.5
2.0 cc	73.5	10.0 cc	68.0
3.0 cc	71.5		
4.0 cc	71.25		
5.0 cc	69.25		
6.0 cc	68.5		
7.0 cc	67.5		

Fig. 8, Curve 2.

Table 12.

30 cc 2.5×10^{-2}M vanadyl chloride against 2×10^{-1}M monoethanolamine.

Vol. of Monoethanolamine	Current (amp. 2.2×10^{-8})	Vol. of Monoethanolamine	Current (amp. 2.2×10^{-8})
0	91.5	12.0 cc	72.0
2.0 cc	90.0	14.0 cc	77.0
4.0 cc	86.0	16.0 cc	76.5
6.0 cc	81.0	18.0 cc	-
8.0 cc	78.5	-	-
10.0 cc	74.0	-	-

Fig. 8, Curve 3.

Spectrophotometric studies on vanadyl chloride and Diethanol amine complex:

Vanadyl chloride found to form a greenish yellow coloured soluble complex with diethanol amine, like monoethanolamine complex, the colour of the complex faded on long exposure to atmosphere, hence all the absorption measurements were made with samples covered with a thin layer of liquid paraffin on their surfaces.

Vosburgh and Cooper's method was again followed to determine the number of complexes formed. Equimolar (1×10^{-2}M) solutions of the reactants viz., vanadyl chloride and diethanolamine were mixed in the ratios of 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 respectively and their absorbances were noted in the wave length range of 400 to 1000 mu.

Table 13.

Concentration of vanadyl chloride = $1x10^{-2}M$

Concentration of Diethanolamine = $1x10^{-2}M$

Wave length (mu)	2: 8 (1)	3: 7 (2)	4: 6 (3)	5: 5 (4)	6: 4 (5)	7: 3 (6)
400	0.110	0.360	0.77	0.90	0.82	0.70
450	0.075	0.310	0.44	0.410	0.380	0.355
500	0.065	0.280	0.295	0.145	0.10	0.080
550	0.060	0.245	0.280	0.105	0.060	0.035
600	0.065	0.215	0.250	0.120	0.085	0.050
625	0.050	0.20	0.235	0.125	0.095	0.055
650	0.050	0.190	0.245	0.120	0.095	0.060
700	0.060	0.185	0.210	0.135	0.100	0.080
725	0.060	0.165	0.20	0.140	0.110	0.080
750	0.60	0.190	0.210	0.150	0.110	0.090
775	0.070	0.20	0.220	0.175	0.120	0.10
800	0.075	0.220	0.240	0.190	0.145	0.110
850	0.070	0.185	0.20	0.155	0.100	0.085
900	0.070	0.185	0.20	0.180	0.105	0.065
950	0.075	0.175	0.20	0.180	0.10	0.055
1000	0.075	0.165	0.210	0.180	0.10	0.040

Fig. 9.

Job's method of continuous variation was employed for determining the composition of the complex. Equimolar solutions of the vanadyl chloride and diethanolamine of concentrations $1x10^{-2}M$, $6.6x10^{-3}M$ and $5x10^{-3}M$ were mixed

according to the method of continuous variation and their absorbances were measured at 800 mu. The absorbances of vanadyl chloride and diethanolamine of the same concentration were also measured. The former showed considerble absorbance but in the latter case there was negligible absorbance.

Table 14.

Set I.

Concentration of vanadyl chloride = $1x10^{-2}M$

Concentration of Diethanolamine = $1x10^{-2}M$

Wave length: 800 mu

Vol. of vanadyl chloride	Vol. of Diethanol amine	O.D.	Vol. of vanadyl chloride	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.070	1 cc	9 cc	0.030	0.040
2 cc	8 cc	0.410	2 cc	8 cc	0.050	0.360
3 cc	7 cc	0.40	3 cc	7 cc	0.10	0.30
4 cc	6 cc	0.350	4 cc	6 cc	0.110	0.240
5 cc	5 cc	0.290	5 cc	5 cc	0.115	0.175
6 cc	4 cc	0.270	6 cc	4 cc	0.150	0.120
7 cc	3 cc	0.235	7 cc	3 cc	0.175	0.065
8 cc	2 cc	0.210	8 cc	2 cc	0.195	0.015
9 cc	1 cc	0.220	9 cc	1 cc	0.220	-

Fig. 10, Curve (1).

Table 15.

Set II.

Concentration of vanadyl chloride = 6.6×10^{-3}M

Concentration of Diethanolamine = 6.6×10^{-3}M

Wave length: 800 mu

Vol. of vanadyl chloride	Vol. of diethanol amine	O.D.	Vol. of vanadyl chloride	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.085	1 cc	9 cc	0.040	0.045
2 cc	8 cc	0.310	2 cc	8 cc	0.055	0.255
3 cc	7 cc	0.305	3 cc	7 cc	0.065	0.240
4 cc	6 cc	0.235	4 cc	6 cc	0.060	0.175
5 cc	5 cc	0.20	5 cc	5 cc	0.075	0.125
6 cc	4 cc	0.170	6 cc	4 cc	0.090	0.080
7 cc	3 cc	0.145	7 cc	3 cc	0.110	0.035
8 cc	2 cc	0.130	8 cc	2 cc	0.115	0.015
9 cc	1 cc	0.130	9 cc	1 cc	0.135	-

Fig. 10, Curve (2)

Table 16.

Set III.

Concentration of Vanadyl chloride = 5×10^{-3}M

Concentration of Diethanolamine = 5×10^{-3}M

Wave length: 800 mu

Vol. of vanadyl chloride	Vol. of diethanol amine	O.D.	Vol. of vanadyl chloride	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.045	1 cc	9 cc	0.010	0.035
2 cc	8 cc	0.130	2 cc	8 cc	0.045	0.095
3 cc	7 cc	0.055	3 cc	7 cc	0.010	0.045
4 cc	6 cc	0.050	4 cc	6 cc	0.020	0.030
5 cc	5 cc	0.060	5 cc	5 cc	0.035	0.025
6 cc	4 cc	0.080	6 cc	4 cc	0.065	0.015
7 cc	3 cc	0.075	7 cc	3 cc	0.065	0.010
8 cc	2 cc	0.10	8 cc	2 cc	0.090	0.10
9 cc	1 cc	0.110	9 cc	1 cc	0.115	-

Fig. 10, Curve (3)

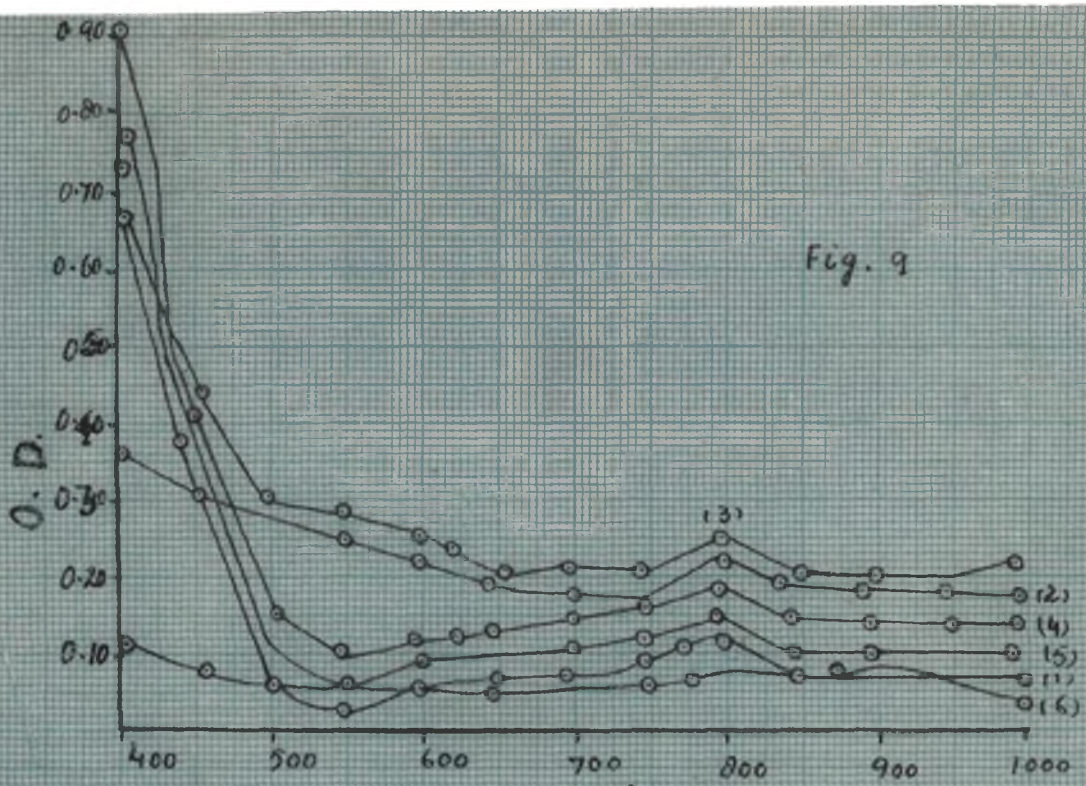


Fig. 9

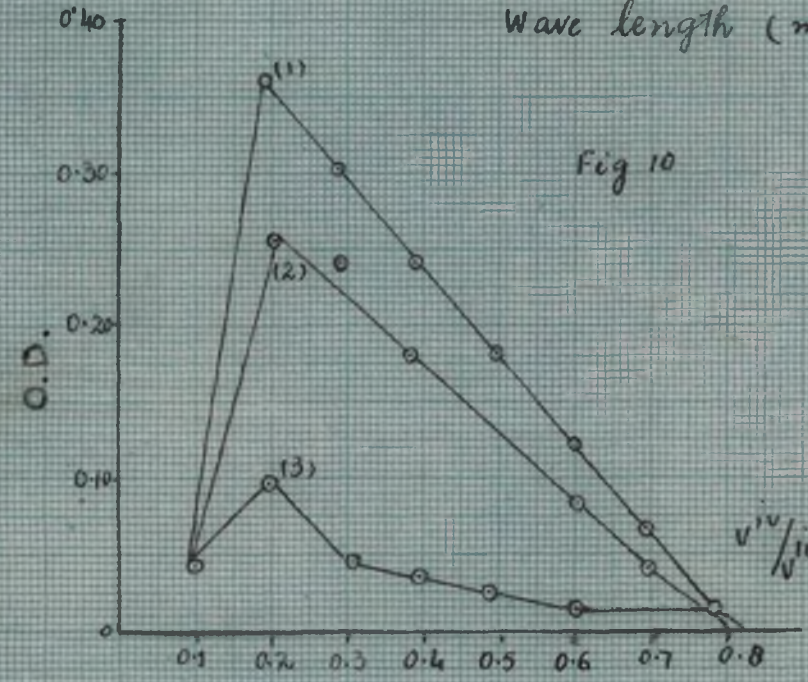


Fig 10

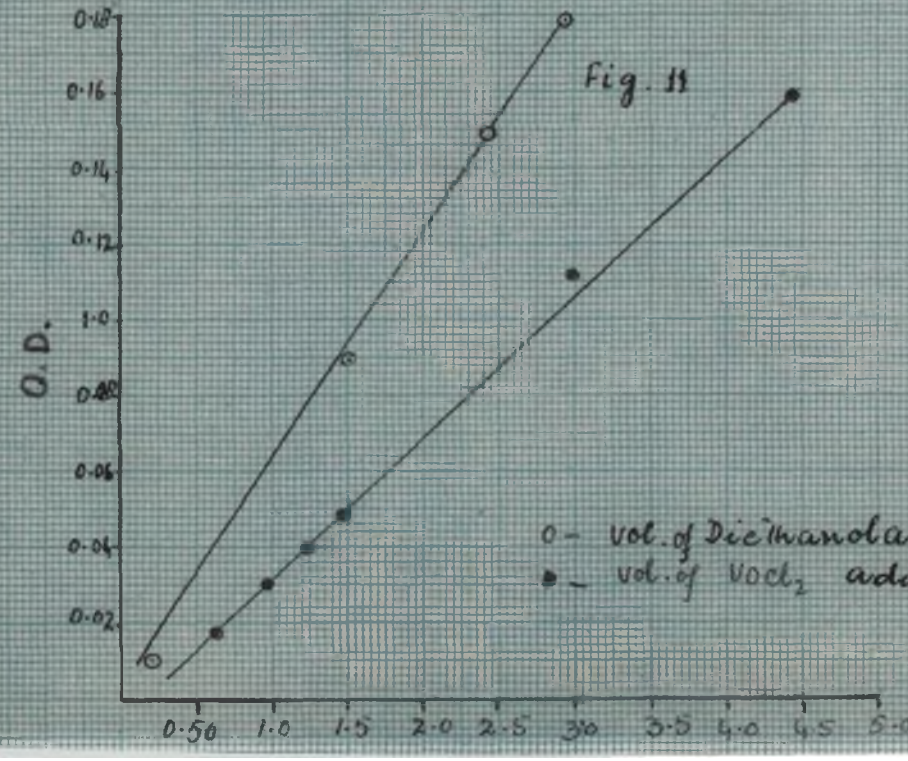


Fig. 11

For the slope ratio method, two sets of experiment were conducted. In the first set the concentration of vanadyl chloride was kept constant and that of diethanolamine was varied, in the other set the mixing was done in the reverse order.

Table 17.

Set I.

Vol. of $2x10^{-2}M$ vanadyl chloride = 0.20 cc

Strength of diethanolamine = $5x10^{-3}M$.

Set II.

Vol. of $2x10^{-2}M$ diethanolamine = 0.2 cc

Strength of vanadyl chloride = $5x10^{-3}M$

The voloume of the solutions (of the set I and II) was diluted to 5.0 cc before performing absorption experiments.

Wave length: 800 mu

Vol. of Diethanolamine	O.D.	Vol. of Vanadyl chloride	O.D.
0 cc	-	0 cc	-
0.2 cc	0.020	0.2 cc	-
0.4 cc	0.0280	0.4 cc	0.008
0.5 cc	0.030	0.5 cc	0.010
0.6 cc	0.040	0.6 cc	-
1.0 cc	0.064	1.0 cc	0.028
1.2 cc	0.080	1.3 cc	0.042
1.5 cc	0.092	1.5 cc	0.050
2.0 cc	0.120	2.0 cc	0.070
2.5 cc	0.150	2.5 cc	0.090
3.0 cc	0.180	3.0 cc	0.11
4.0 cc	-	3.5 cc	0.120
4.5 cc	-	4.0 cc	0.140
		4.5 cc	0.160

Fig. 11, Curve (1) Fig. 11, Curve (2)

The absorbances of mixtures of 5×10^{-3}M vanadyl chloride and diethanolamine (mixed in the ratio of 1:4) at different pH's were measured at various wave lengths (400 to 1000 mu). The data are given in the following table.

Table 18.

Concentration of Vanadyl Chloride = 5×10^{-3}M

Concentration of Diethanolamine = 5×10^{-3}M

Wave length m.u.	pH = 4.0 (1)	pH = 4.9 (2)	pH = 5.5 (3)	pH = 6.6 (4)	pH = 6.8 (5)	pH = 7.4 (6)	pH = 8.3 (7)	pH = 9.0 (8)	pH = 10.9 (9)	pH = 11.4 (10)
400	0.460	0.960	0.740	0.235	0.135	0.110	0.120	0.56	0.215	0.250
450	0.215	0.550	0.440	0.120	0.055	0.045	0.075	0.395	0.165	0.205
500	0.125	0.420	0.325	0.105	0.050	0.040	0.060	0.325	0.120	0.15
550	0.135	0.395	0.310	0.125	0.045	0.045	0.070	0.30	0.115	0.135
600	0.165	0.420	0.340	0.155	0.075	0.065	0.080	0.285	0.095	0.110
650	0.210	0.440	0.380	0.165	0.090	0.085	0.060	0.205	0.090	0.090
700	0.270	0.500	0.420	0.185	0.080	0.080	0.060	0.205	0.090	0.085
750	0.350	0.530	0.445	0.205	0.085	0.080	0.065	0.210	0.090	0.080
800	0.325	0.530	0.445	0.300	0.120	0.10	0.075	0.230	0.10	0.120
850	0.340	0.520	0.430	0.250	0.085	0.070	0.070	0.20	0.085	0.10
900	0.345	0.520	0.430	0.230	0.090	0.040	0.070	0.190	0.080	0.095
950	0.355	0.520	0.430	0.220	0.090	0.065	0.070	0.190	0.080	0.090
1000	0.310	0.470	0.395	0.20	0.075	0.060	0.070	0.190	0.075	0.090

Fig. 12.

Amperometric Titrations:

Amperometric titrations between vanadyl chloride (in the cell) and diethanolamine were carried out in a similar manner as in case of vanadyl- monoethanolamine complexes.

Direct

1. 5.0 cc of 5 $x10^{-2}$M vanadyl chloride + 10 cc H_2SO_4 ($2x10^{-1}$M) + 2.0 cc gelatin ($1x10^{-10}$%) + 13 cc H_2O against 2 $x10^{-M}$ diethanolamine.

2. 10.0 cc of 5 $x10^{-2}$M vanadyl chloride + 10 cc H_2SO_4 (2 $x10^{-1}$M) + 2.0 cc gelatin ($1x10^{-1}$%) + 8 cc H_2O against 2 $x10^{-1}$M diethanolamine.

3. 15.0 cc of 5 $x10^{-2}$M vanadyl chloride + 10 cc H_2SO_4 gSO^ (2 $x10^{-1}$M) + 2.0 cc gelatin ($1x10^{-1}$%) + 3 cc H_2O against 2 $x10^{-1}$M diethanolamine.

Table 19.

30 cc of $8.3x10^{-3}$M vanadyl chloride against 2 $x10^{-1}$M diethanolamine.

Voltage applied:- 1.0 Volt.

Vol. of Diethanolamine	Current (amp. 2.2 $x10^{-8}$)	Vol. of Diethanol amine	Current (amp. 2.2$x10^{-8}$)
0	57.5	8.0 cc	38.0
1.0 cc	53.0	9.0 cc	33.0
2.0 cc	48.5	10.0 cc	31.5
3.0 cc	45.5		
4.0 cc	42.5		
5.0 cc	40.0		
6.0 cc	38.0		
7.0 cc	36.0		

Fig. 13, Curve (1)

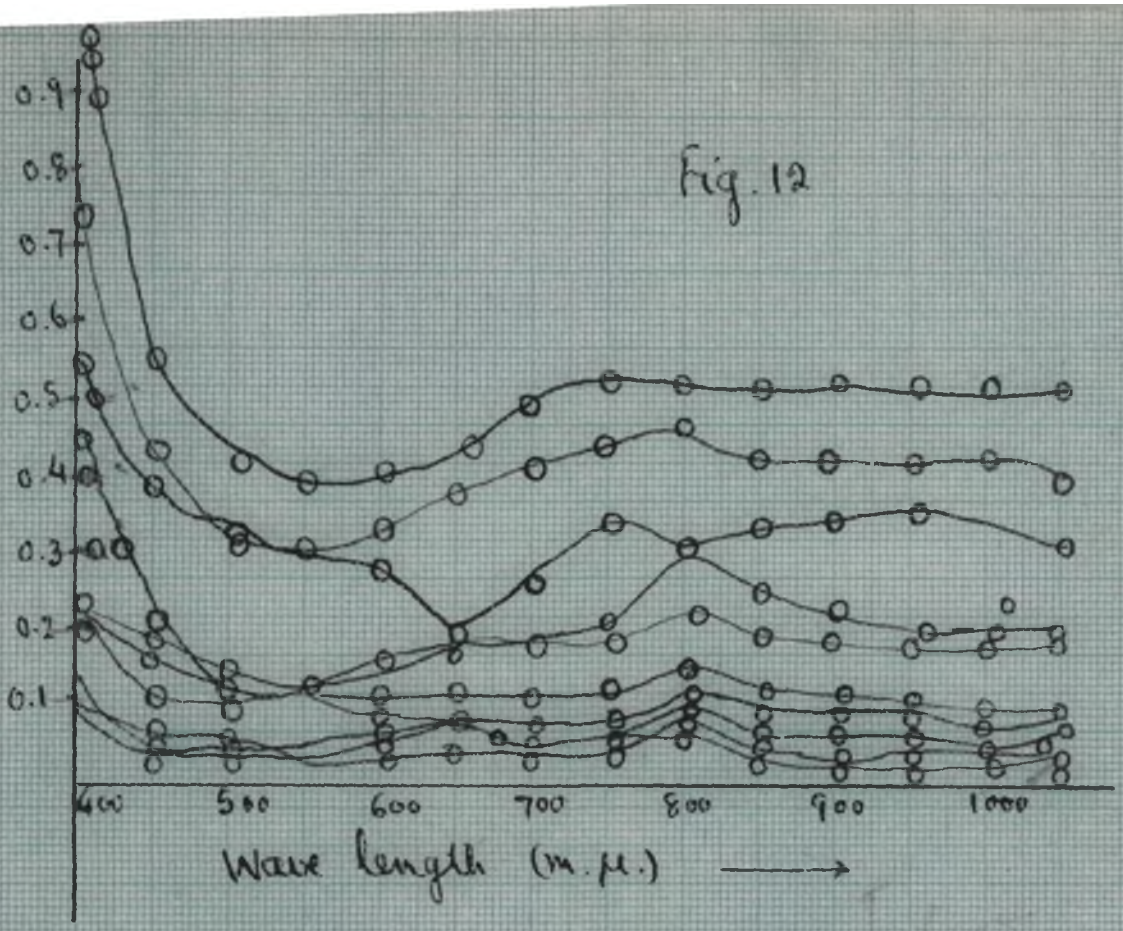

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
400
500
600
700
800
900
1000
Wave length (m.μ.) ——→

Fig. 12

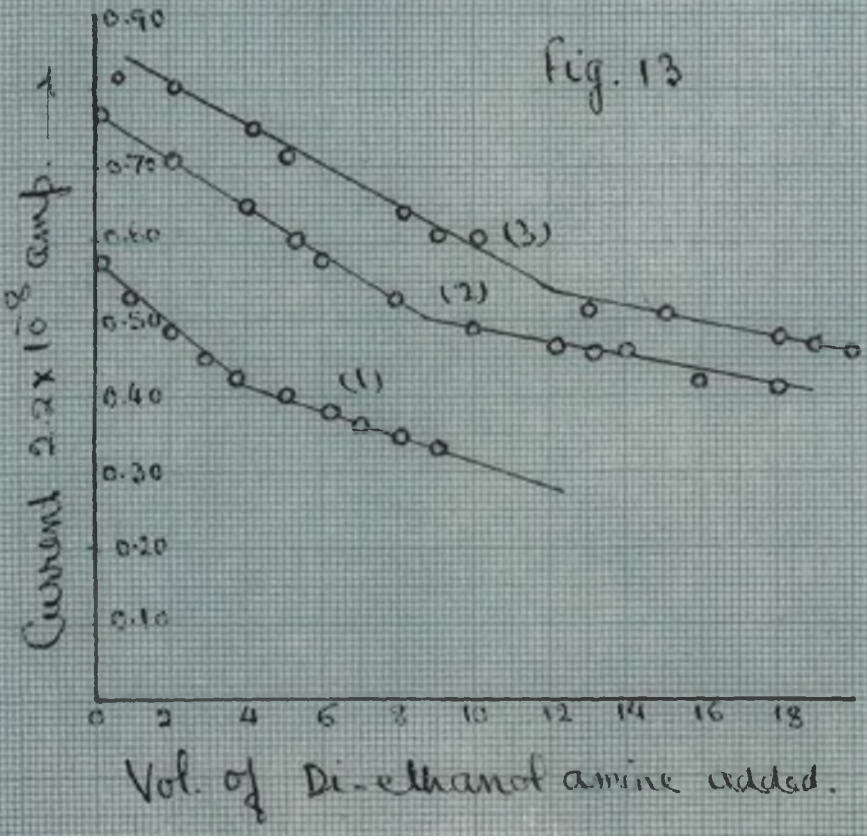

0.90
0.70
0.60
0.50
0.40
0.30
0.20
0.10
(3)
(2)
(1)
0 2 4 6 8 10 12 14 16 18
Vol. of Di-ethanol amine added.

Fig. 13

Table 20.

30 cc, 1.66 $x10^{-2}$M vanadyl chloride against 2 $x10^{-1}$M diethanolamine.

Voltage applied:- 1.0 Volt.

Vol. of Diethanol-amine	Current (amp. $2.2x10^{-8}$)	Vol. of Diethanol-amine	Current (amp. $2.2x10^{-8}$)
0 cc	76.5	10.0 cc	48.5
2.0 cc	70.0	12.0 cc	46.5
4.0 cc	64.0	13.0 cc	46.5
5.0 cc	60.0	14.0 cc	46.0
6.0 cc	58.0	16.0 cc	42.5
8.0 cc	52.5	18.0 cc	41.0
9.0 cc	50.0		

Fig. 13, Curve (2).

Table 21.

30 cc 2.5 $x10^{-2}$M vanadyl chloride against $2x10^{-1}$M diethanolamine.

Voltage applied:- 1.0 Volt.

Vol. of Diethanol-amine	Current (amp. $2.2x10^{-8}$)	Vol. of Diethanol-amine	Current (amp. $2.2x10^{-8}$)
0 cc	86.5	14.0	52.5
2.0 cc	80.0	15.0	50.5
4.0 cc	75.0	16.0	51.0
5.0 cc	70.5	17.0	48.0
6.0 cc	70.0	18.0	48.5
8.0 cc	64.0	20.0	45.5
10.0 cc	59.5		
12.0 cc	53.5		

Fig. 13, Curve (3).

Spectro-photometric studies on Vanadyl chloride and Tri-ethanolamine complex:

A greenish yellow coloured complex was formed by the interaction of vanadyl chloride and triethanolamine. The colour of the complex faded on long exposure to air, however, on keeping a thin layer of liquid paraffin on its surface it remained stable for many days. Hence all the absorption measurements were carried under the conditions described in case of mono-and di-ethanolamine complexes.

Spectrophotometric studies on Vanadyl-Triethanolamine complex:

Vosburgh and Cooper's method was applied to know the number of complexes formed in the solution. Equimolar solutions of vanadyl chloride and triethanolamine of concentration 1 $x10^{-2}$M were mixed respectively in the ratio of 2:8, 3:7, 4:6, 5:5, 6:4 and 7:3 and their O.D. were measured in the wave length range of 400 to 1000 mu.

Table 22.

Concentration of Vanadyl chloride = 1×10^{-2}M

Concentration of triethanolamine = 1×10^{-2}M

Wave length mu	2 : 8 (1)	3 : 7 (2)	4 : 6 (3)	5 : 5 (4)	6 : 4 (5)	7 : 3 (6)
400	0.065	0.440	0.640	0.84	0.63	0.72
450	0.035	0.390	0.350	0.375	0.245	0.05
500	0.060	0.385	0.255	0.105	0.260	0.055
550	0.055	0.330	0.245	0.065	0.270	0.030
600	0.055	0.240	0.255	0.085	0.290	0.025
650	0.060	0.250	0.250	0.095	0.30	0.045
700	0.070	0.240	0.265	0.120	0.320	0.055
750	0.080	0.210	0.280	0.130	0.340	0.075
800	0.10	0.250	0.30	0.140	0.350	0.085
850	0.080	0.190	0.260	0.115	0.320	0.065
900	0.070	0.175	0.210	0.115	0.320	0.075
950	0.050	0.170	0.20	0.110	0.320	0.040
1000	0.040	0.175	0.180	0.10	0.320	0.045

Fig. 22.

The composition of the vanadyl triethanolamine complex was determined by Job's method. Equimolar solutions of the reactants viz., vanadyl chloride and triethanolamine of concentrations 2×10^{-2}M; 1.33×10^{-2}M and 1×10^{-2}M were mixed according to the method of continuous variations and their O.D. were measured at 800 mu. The absorbances of triethanol amine and vanadyl chloride of the same concentrations were also measured. Triethanol amine showed negligible absorption at this wave length, but vanadyl chloride had considerable absorption. VO^{++}/VO^{++} + T.A. was plotted against diff in optical densities.

Table 23.

Concentration of vanadyl chloride = 2×10^{-2}M

Concentration of Tri ethanol amine = 2×10^{-2}M

Wave length : 800 mu

Vol. of $VoCl_2$	Vol. of Tri ethanol amine	O.D.	Vol. of $VoCl_2$	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.125	1 cc	9 cc	0.080	0.045
2 cc	8 cc	0.480	2 cc	8 cc	0.140	0.340
3 cc	7 cc	0.710	3 cc	7 cc	0.120	0.590
4 cc	6 cc	0.970	4 cc	6 cc	0.170	0.80
5 cc	5 cc	0.82	5 cc	5 cc	0.215	0.605
6 cc	4 cc	0.7	6 cc	4 cc	0.270	0.370
7 cc	3 cc	0.490	7 cc	3 cc	0.310	0.110
8 cc	2 cc	0.410	8 cc	2 cc	0.350	0.060
9 cc	1 cc	0.370	9 cc	1 cc	0.410	0.040

Fig. 23, Curve 1.

Table 24.

Concentration of Vanadyl chloride = 1.33×10^{-2}M

Concentration of tri ethanol amine = 1.33×10^{-2}M

Wave length : 800 mu

Vol. of $VoCl_2$	Vol. of Triethanol amine	O.D.	Vol. of $VoCl_2$	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.110	1 cc	9 cc	0.020	0.090
2 cc	8 cc	0.260	2 cc	8 cc	0.060	0.20
3 cc	7 cc	0.385	3 cc	7 cc	0.085	0.30
4 cc	6 cc	0.515	4 cc	6 cc	0.110	0.405
5 cc	5 cc	0.440	5 cc	5 cc	0.140	0.30
6 cc	4 cc	0.325	6 cc	4 cc	0.175	0.150
7 cc	3 cc	0.270	7 cc	3 cc	0.210	0.060
8 cc	2 cc	0.255	8 cc	2 cc	0.235	0.020
9 cc	1 cc	0.260	9 cc	1 cc	0.265	-

Fig. 23, Curve 2.

Table 25.

Concentration of Vanadyl chloride = 1×10^{-2}M

Concentration of Tri ethanol amine = 1×10^{-2}M

Wave length : 800 mu

Vol. of $VoCl_2$	Vol. of Triethanol amine	O.D.	Vol. of $VoCl_2$	Vol. of H_2O	O.D.	Diff. in O.D.
1 cc	9 cc	0.095	1 cc	9 cc	0.015	0.080
2 cc	8 cc	0.160	2 cc	8 cc	0.040	0.120
3 cc	7 cc	0.255	3 cc	7 cc	0.055	0.20
4 cc	6 cc	0.375	4 cc	6 cc	0.080	0.295
5 cc	5 cc	0.240	5 cc	5 cc	0.110	0.130
6 cc	4 cc	0.150	6 cc	4 cc	0.130	0.020
7 cc	3 cc	0.175	7 cc	3 cc	0.155	0.020
8 cc	2 cc	0.185	8 cc	2 cc	0.175	0.010
9 cc	1 cc	0.190	9 cc	1 cc	0.195	-

Fig 23, Curve 3.

The composition of the complex was also determined by the slope ratio method.

Table 26.

Set I.

Vol. of 2×10^{-2}M $VoCl_2$ = 0.2 cc

Strength of Triethanolamine = 5×10^{-3}M

Set II.

Vol. of 2×10^{-2}M Triethanolamine = 0.2 cc

Strength of $VoCl_2$ = 5×10^{-3}M

Fig. 22

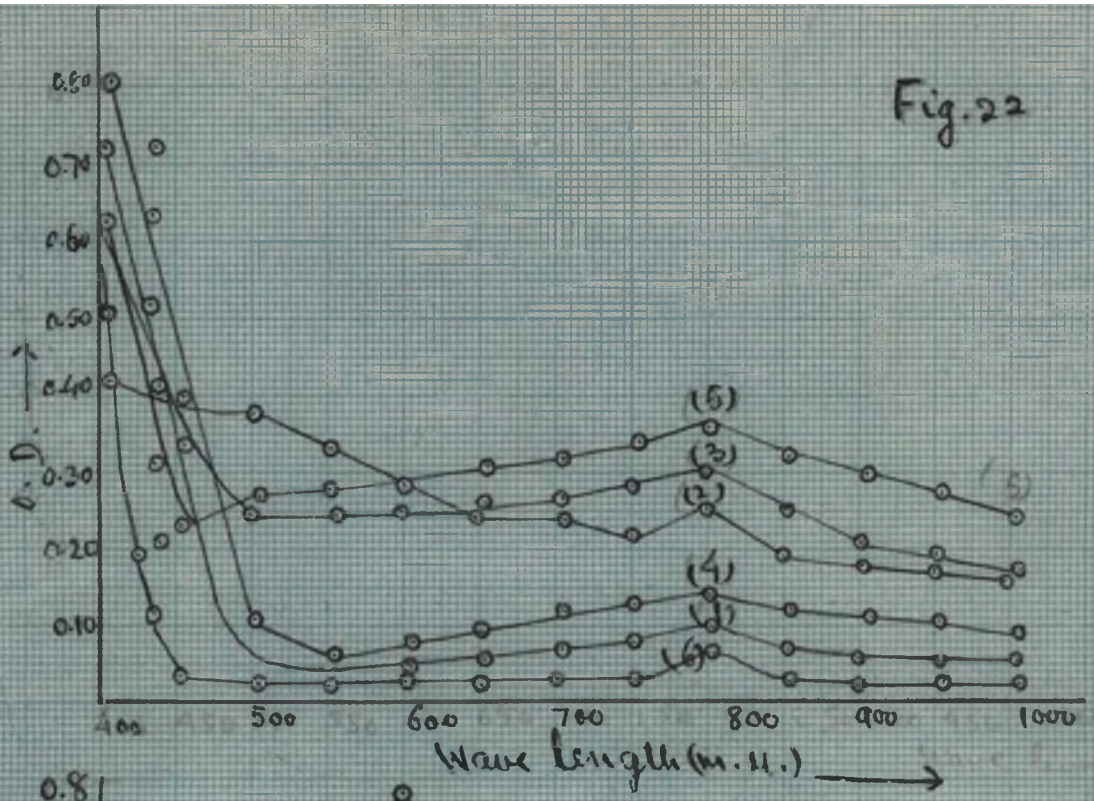


Fig 23

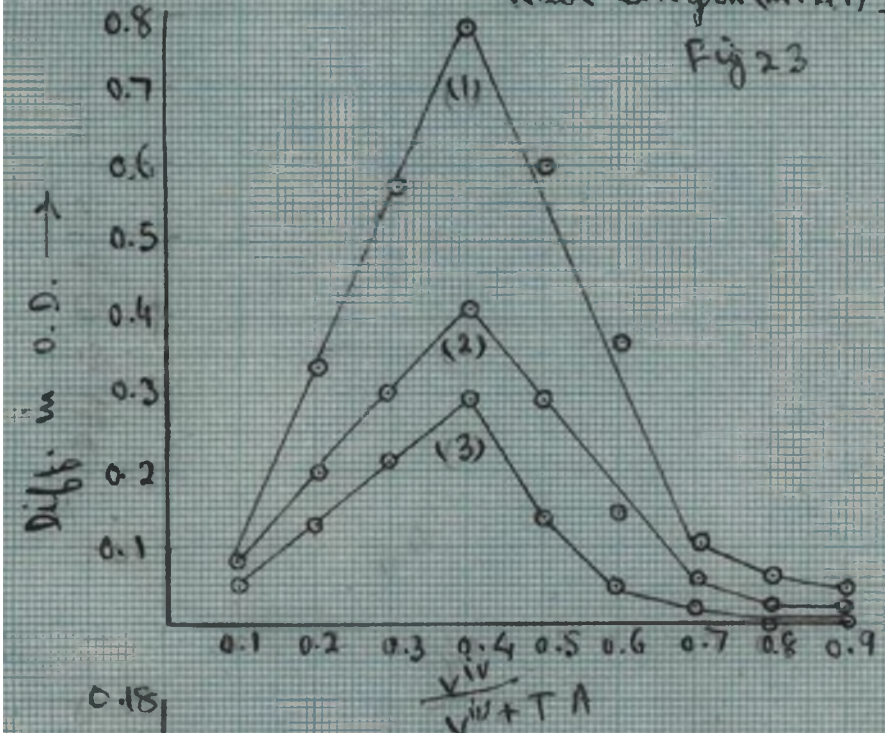
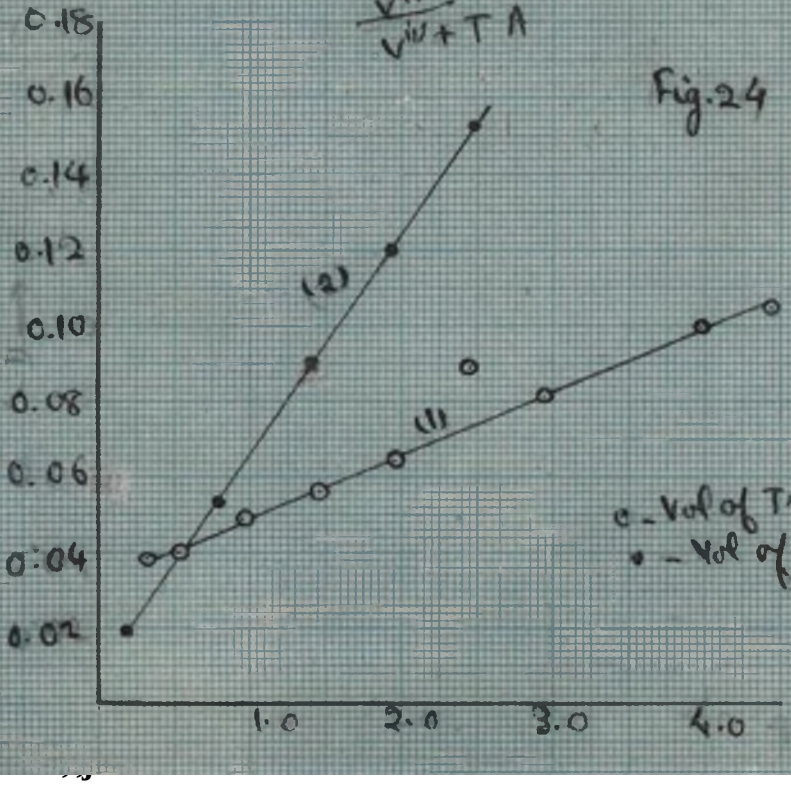


Fig. 24



All the solutions of the Set I and II were diluted to 5.0 cc before O.D. measurements.

Wave length : 800 mu

Set I.		Set II.	
Vol. of Triethanol amine added	O.D.	Vol. of $VoCl_2$ added	O.D.
0.4 cc	0.04	0.2 cc	0.020
0.6 cc	0.045	0.5 cc	0.028
1.0 cc	0.050	0.8 cc	0.055
1.5 cc	0.058	1.0 cc	0.050
2.0 cc	0.065	1.5 cc	0.090
2.5 cc	0.090	2.0 cc	0.120
3.0 cc	0.080	2.5 cc	0.150
3.5 cc	0.088		
4.0 cc	0.096		
4.5 cc	0.104		

Fig. 24, Curve 1 Fig. 24, Curve 2.

The effect of pH on the absorption of the complex was studied quantitatively. Solutions of vanadyl chloride and triethanolamine of concentration $1x10^{-2}M$ were mixed in the ratio of 2:3 respectively and their absorbances were measured in the pH range 4 to 14 and wave length range 400 to 1000 mu.

Table 27.

Concentration of vanadyl chloride = $1 x10^{-2}M$

Concentration of triethanolamine = $1 x10^{-2}M$

Wave length mu	pH = 4.0 (1)	pH = 4.9 (2)	pH = 6.6 (3)	pH = 6.9 (4)	pH = 8.3 (5)	pH = 9.0 (6)	pH = 10.9 (7)	pH = 11.4 (8)
400	0.225	0.73	0.45	0.270	0.20	0.75	0.53	0.85
450	0.10	0.450	0.270	0.180	0.085	0.42	0.320	0.75
500	0.085	0.395	0.235	0.130	0.060	0.280	0.180	0.65
550	0.125	0.395	0.265	0.150	0.075	0.205	0.170	0.575
600	0.170	0.430	0.305	0.190	0.095	0.160	0.050	0.510
625	0.190	0.395	0.30	0.205	0.10	0.130	0.055	0.430
650	0.20	0.410	0.305	0.250	0.105	0.130	0.060	0.470
700	0.240	0.40	0.295	0.260	0.110	0.125	0.085	0.460
725	0.255	0.40	0.305	0.270	0.130	0.130	0.090	0.450
750	0.265	0.410	0.295	0.280	0.130	0.130	0.095	0.480
800	0.275	0.425	0.305	0.300	0.135	0.150	0.085	0.490
850	0.280	0.440	0.340	0.320	0.140	0.175	0.120	0.540
875	0.285	0.430	0.260	0.310	0.135	0.160	0.110	0.530
900	0.270	0.420	0.255	0.290	0.120	0.145	0.10	0.52
1000	0.20	0.40	0.210	0.270	0.085	0.110	0.070	0.48

Fig. 25.

The formation constant of the vanadyl-Triethanolamine complex was determined according to the method of Tanaka and Takamura (Vide page 123 Chapter III).

Optical density measurements for VO^{++} + triethanolamine mixtures made by varying the concentration of VO^{++} and triethanolamine upto 2.5×10^{-3}M in presence of higher concentration of VO^{++} and triethanolamine (8×10^{-3}M) respectively showed that Beer's law is obyed under these conditions. Another set of experiments was carried out by varying the concentration of VO^{++} from 5×10^{-4}M to 3.5×10^{-3}M in presence of low concentration of triethanolamine (8×10^{-4}M) (Fig. 24. Curve 2). The results are given in table 28 and the values of $ab/_D$ are plotted against the concentration of VO^{++} in Fig. 6 b.

Table 28.

Conct. of $VO^{++} \times 10^{-3}$M	D observed	$ab/_D \times 10^{-5}$
(a)		
0.5 cc	0.028	1.43
0.8 cc	0.055	1.16
1.0 cc	0.050	1.60
1.5 cc	0.090	1.33
2.0 cc	0.120	1.33
2.5 cc	0.150	1.33
3.0 cc	0.230	1.08

Fig. 6 b.

Amperometric Titrations: Amperometric titrations between triethanoline amine and vanadyl chloride (in the cell) were carried out in exactly the same manner as in case of mono- and di ethanol amine complexes. Following sets of experiments were planned.

Set I.

5 cc VO^{++} of concentration 5×10^{-2}M + 10 cc H_2SO_4 (2×10^{-1}M) + 2 cc gelatine + 13 cc H_2O against 1×10^{-1}M triethanolamine (1×10^{-10}%)

Set II.

10 cc VO^{++} of concentration 5×10^{-2}M + 10 cc H_2SO_4 + 2 cc (1×10^{-1}%) + 8 cc H_2O against 1×10^{-1}M triethanolamine.

Set III.

5 cc VO^{++} of concentration 5×10^{-2}M + 10 cc H_2SO_4 (2×10^{-1}M) + 2 cc gelatin + 13 cc H_2O against 8.3×10^{-2}M triethanolamine.

Direct titrations: Vanadyl chloride in the cell.

Fig. 25

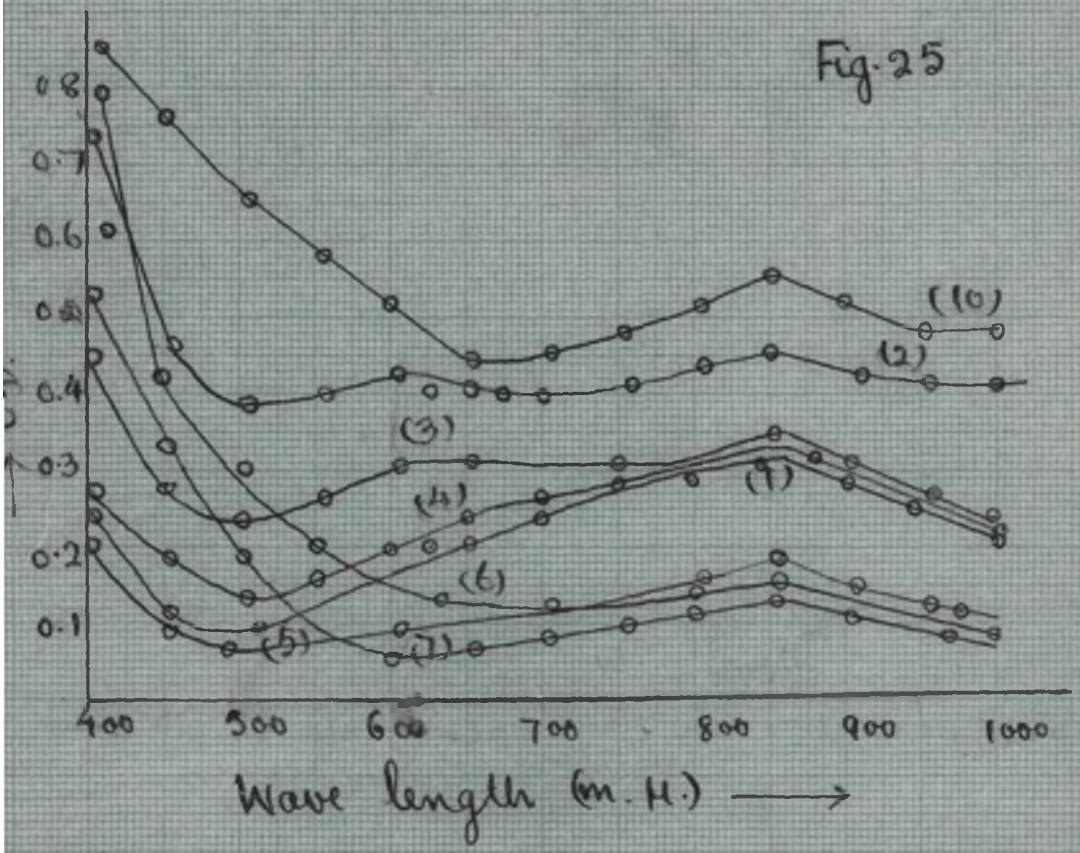

0·8
0·7
0·6
0·4
0·3
0·2
0·1
(10)
(2)
(3)
(4)
(7)
(6)
(5)
(1)
400
500
600
700
800
900
1000
Wave length (m. μ.) ⟶

Fig. 26

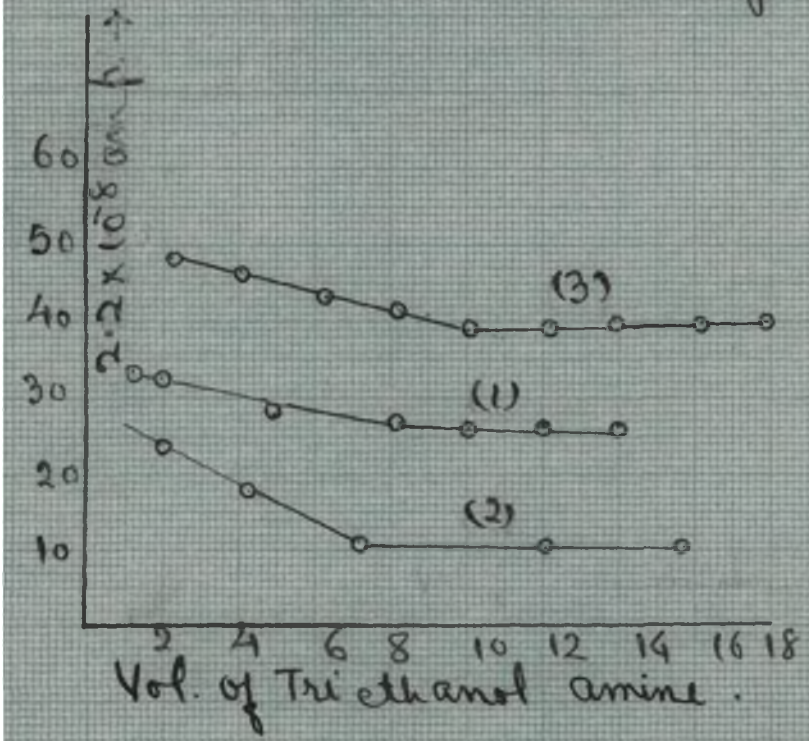

60
50
40
30
20
10
(3)
(1)
(2)
2
4
6
8
10
12
14
16
18
Vol. of Triethanol amine.

Table 31.

Set III.

30 cc 8.3×10^{-3}M vanadyl chloride against 8.3×10^{-2}M triethanolamine.

Vol. of triethanol-amine	Current 2.2×10^{-4} amp.	Vol. of triethanol-amine	Current 2.2×10^{-4} amp.
1.0 cc	34.5	7.0 cc	27.5
2.0 cc	33.5	8.0 cc	27.0
4.0 cc	30.0	9.0 cc	26.25
5.0 cc	29.0	10.0	26.5
6.0 cc	28.0		

Fig. 26, Curve (1)

D I S C U S S I O N

Preliminary experiments with all the three amines gave the following information regarding the complexes.

(i) The reaction was possible only in concentrated solutions (2×10^{-2}M to 5×10^{-3}M). In more concentrated solutions a turbidity was found to set in.

(ii) The colour of the complexes faded on long exposure to air. However, on keeping a layer of liquid paraffin on their surfaces, the colour of the solution remained as such for several days.

(iii) The complexes crystallised in well defined black products these were extremely hygroscopic in nature but were found to be quite stable.

Vanadyl chloride- Monoethanolamine complex:

The spectrophotometric studies gave the following information regarding the composition of the complex.

(i) Vosburgh and Cooper's method followed to determine the number of complexes formed showed the existence of only one complex, whose maxima lies at 650 mu (Table 2, Fig. 1).

(ii) Job's method of continuous variation applied for determining the composition of the complex gave indication for a 2:3 vanadyl and monoethanolamine complex.

The results are tabulated below.

Table 32.

Fig. No.	Curve No.	Concentration of VO^{++} and monoethanol-amine	Wave length	Composition of the complex VO^{++} mono-ethanolamine
3	(1)	2 $x10^{-2}$M	650	2: 3
3	(2)	1 $x10^{-2}$M	650	2: 3
3	(3)	5 $x10^{-3}$M	650	2: 3

(iii) The results obtained by the method of continuous variation were furthur confirmed by the slope ratio method the ratio obtained from the slopes over the st. line portion of the curves (Fig. 4, Curve (1) and (2). Table 6) was found to be 2: 3 for vanadyl chloride and monoethanolamine.

(iv) The effect of pH (4.0 to 11.4) on the absorption of the complex studied quantitatively, showd that a max was indicated at 650 mu in the pH range 6.6 to 11.4, no maxima was realised at pH below 6.6 (Fig. 5. Table 7). This indicates that the complex was stable in the pH range 6.6 to 11.4.

(v) The value of the formation constant for the vanadyl-monoethanolamine complex was found out by the method of Tanaka and Takamura. On plotting $ab/_D$ against a, a straight line was obtained (Fig. 6a, Table 8) having a slope of 1.25×10^{-2}M the value of E and $\frac{1}{EK}$ obtained were 2.4×10^{-2} and 6.1×10^{-5} respectively, hence the value of formation constant K was estimated to be $6.8 \times 10^{+4}$. The amperometric titrations gave the following information regarding the composition of the complex.

The complex was found to be non reducible at the dropping mercury electrode, hence polarography of the complex could not be carried out. However, amperometry was found to be quite suitable for investigating the composition of the complex . Polarogram of vanadyl chloride (4×10^{-4}M) in sulphuric acid (8×10^{-2}M) (Fig. 7. Table 9) gave a value of - 1.0 volt to be applied for the amperometri studies.

The results obtained by the amperometric titrations of vanadyl chloride (in the cell) against monoethanolamine are summarised in the following table.

Table 33.

Fig. No.	Curve No.	Vol. of vanadyl chloride	Vol. of monoethanolamine	Ratio from the point of inflexion VO^{++} monoethanolamine
6	(1)	5.0cc(5.0×10^{-2}M)	2.8cc(2.0×10^{-2}M)	1:2.20
6	(2)	10.0cc(5.0×10^{-2}M)	5.1cc(2.0×10^{-2}M)	1:2.04
6	(3)	15.0cc(5.0×10^{-2}M)	8.4cc(2.0×10^{-2}M)	1:2.20

The amperometric titrations carried out between monoethanolamine (in the cell) and vanadyl chloride as titrant did not prove successfull and no significant inflexions point was observed in these cases.

On the basis of amperometric studies, the formula of the complex may be written as

$$NH_2.\ C_2H_4OH - VO^{++} - HO\ C_2H_4\ NH_2$$

Vanadyl chloride- Diethanolamine complex:

Spectrophotometric studies provide the following information regarding the composition of the complex.

(i) Vosburgh and Cooper's method followed to determiermiE the number of complexes formed by the interaction of diethanolamine and vanadyl chloride show that all the

mixures gave a maximum at 800 mu, indicating thereby the formation of only one complex (Table 13, Fig. 9).

(ii) On plotting the optical densities of the solutions (prepared according to the method of continuous variation) against the ratio $\frac{VO^{++}}{VO^{++} D.E}$ a combining ratio of 1: 4 for VO^{++} to diethanolamine was obtained. The results of Job's method are summarised as follows.

Table 34.

Fig. No.	Curve No.	Conc. of VO^{++} and diethanol-amine	Wave length	Composition of the complex VO^{++} diethanolamine
10	(1)	1 $x10^{-2}$M	800 mu	1: 4
10	(2)	6.6 $x10^{-3}$M	800 mu	1: 4
10	(3)	5 $x10^{-3}$M	800 mu	1: 4

(iii) In order to confirm the results obtained by the the Job's method, the slope ratio method was also conducted. From the slopes, determined from the straight line portion of the curves (Fig. 11. Table 17) a ratio of 2:3 for VO^{++} to diethanolamine was obtained.

From the above results it may be concluded that no conclusive information was obtained by the spectrophotometric methods regarding the composition of the complex.

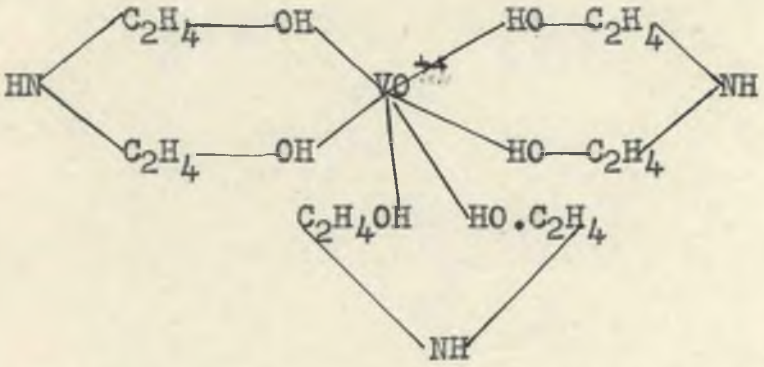
(iv) Absorption experiments carried out at different pH's (4.0 to 11.4) and varying wave lengths (400 to 1000 mu) showed the existence of a maxima at 800 mu in the pH range 6.6 to 11.4, indicating thereby the stability of the complex in this pH range (Fig. 12, Table 18).

Amperometric titrations carried out between di ethanol amine and vanadyl chloride (in the cell) at - 1.0V gave the information of 1:3 for VO^{++} to di ethanol amine complex. The results are tabulated as follows:

Table 35.

Fig. No.	Curve No.	Vol. of Vanadyl chloride	Vol. of di ethanol amine	Ratio the information point VO^{++} : di ethanol amine
13	(1)	5.0 cc (5×10^{-2}M)	3.7 cc (2×10^{-1}M)	1 : 3
13	(2)	10.0 cc (5×10^{-2}M)	8.8 cc (2×10^{-1}M)	1 : 3
13	(3)	15.0 cc (5×10^{-2}M)	12.0 cc (2×10^{-1}M)	1 : 3

On the basis of the information obtained by the amperometric studies, the following structure may be assigned to the complex.



Vanadyl Chloride - Tri ethanol amine Complex.

The spectrophotometric carried out to investigate the composition of the complex, gave the following information.

(i) The absorption spectra of equimolar solutions vanadyl chloride and tri ethanol amine, mixed in the ratio of 2 : 8, 3 : 7, 4:6, 5:5, 6:4 and 7:3 respectively studied in the range of 400 - 1000 mu indicate a single maxima at 800 mu indicating thereby the existence of only one complex (Table 22, Fig. 22).

(ii) Job's method of continuous variation applied for elucidating the composition of the complex gave indication for a 2:3 complex. The results are

summarised in the following table:

Table 36

Fig. No.	Curve No.	Conc. of VO^{++} and tri ethanol amine	Wave length	Composition of complex VO^{++} : tri ethanol amin
23	(1)	2.0×10^{-2} M	800 mu	2 : 3
23	(2)	1.33×10^{-2} M	800 mu	2 : 3
23	(3)	1×10^{-2} M	800 mu	2 : 3

(iii) The results obtained by the Job's method were further confirmed by the slope ratio method. The ratio of the slopes determined from the straight line portion of the curves (Table 26, Fig. 24) provided information for a 2 : 3 complex (VO^{++}: tri ethanol amine).

The absorption of the solutions (obtained by mixing the equimolar solutions of the reactants in the ratio of 2 : 3) measured in the pH range 4 to 11.6, showed the single absorption peak at 850 mu in the pH range of 5.5 to 11.6, indicating thereby the existence of a complex in this pH range (Fig. 25).

The formation constant was calculated in the similar manner as in case of di ethanol amine. The rectilinear curve

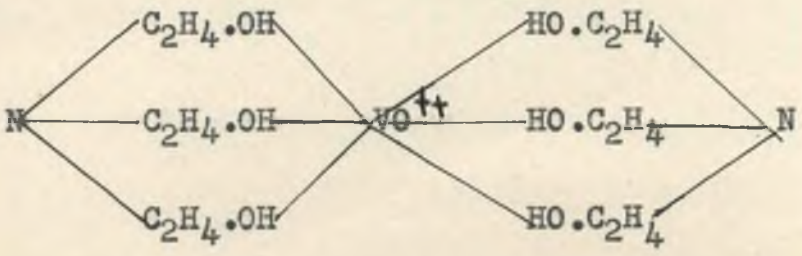
obtained by plotting $ab/_D$ against a, gave value of slope as 1.25×10^{-2} and that of molar extinction coefficient 2.4×10^{-2}. The value of formation constant K worked out thereby to be 2.94×10^{4} (Fig. 6b, Table 28).

The amperometric titrations carried out between vanadyl chloride (in the cell) and tri ethanol amine indicate the formation of 1: 2 complex. The results are summarised in the following table:

Table 37.

Fig.No.	Curve No.	Vol. of vanadyl chloride	Vol. of tri ethanol amine	Ratio from the point of inflexion VO^{++} : tri ethanol ami
26	(1)	5.0 cc (5×10^{-2}M)	5.0 cc(8.3×10^{-2}M)	1 : 2.0
26	(2)	5.0 cc (5×10^{-2}M)	7.0 cc(7.5×10^{-2}M)	1 : 2.1
26	(3)	10.0 cc (5×10^{-2}M)	10.0 cc(1 $\times 10^{-2}$M)	1 : 2.04

On the basis of amperometric studies the structural formula of the complex may be written as



The most striking feature of the vanadyl - Ethanolamines reaction, is that the different spectrophotometric studies give such ratios which do not lead to precise knowledge about the composition of the complexes formed. On the other hand, the amperometric studies had been able to give the desired information. The discrepancy in the results of the two methods might be attributed to two factors (i) Instability of the complexes under ordinary atmmspheric conditions and (ii) the presence of colloidal precipitates. With these limitations, the spectrophotometric method is liable to give less reliable results. In the amperometric titrations these difficulties could easily be overcome, particularly the former one since all measurements were carried out in an atmosphere of nitrogen.

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C H A P T E R V.

Interaction of Cr(ii and iii) with Hydrazine.

INTERACTION OF Cr(ii and iii) WITH HYDRAZINE

Hydrazine enters into complex formation with a number of metal ions. However, the number of complexes are limited because of the highly reducing action of hydrazine.[1] Generally it does not form stable complexes with noble metals or with metals in their higher oxidation states. Audrieth[2] made a systematic study of the hydrazine complexes. According to him, in most cases the hydrazine molecule coordinates to the metal ion through nitrogen and the number of coordinating molecules is half the coordination number usually assigned to a metal ion. A large number of metals including those of transitional series interact with hydrazine forming complexes. Worthmentioning are the complexes of Pt(ii), Pt(iv)[3], Ni[4], Tl(iii)[5], Zn[6], Ru[7], Cu(ii)[8], Ag[9], Hg[10] and Cr(ii)[11]. These complexes may be divided into two catagories.

(i) Simple addition compounds e.g. $AgCl.N_2H_4$, $HgCl_2.N_2H_4$ etc. and (ii) coordination or chelate complexes e.g. complex of Pt, Ni, Cr, Cu etc. In most cases there is not enough of hydrazine to fill the coordination sphere, hence it has been suggested that it acts as a bidentate, forming a three membered ring. Goremykin[12] showed that in platinum complexes hydrazine acted as a monodentate donor. Further evidence was obtained by the work of Robertus, Lactinen and Bailar[13] and Schwarzenbach and Zobist[14]. On the basis of polarographic

studies, showed the formation of titrahydrazinate of zinc in solution where the metal coordinates to four hydrazine molecules with only small difference between the dissociation constants. Schwarzenbach[14] showed that 4 hydrazine molecules are bound to Zn (ii) ion and six to Ni (ii) ion, comparable to the binding of ammonia to these metals. From the existing evidences available the presence of three membered ring is rather doubtful.

Of the large number of metal hydrazine complexes quoted in the literature, those of Cr (ii) have not been fully investigated. Traube and Passarge[15] on the basis of the results on chemical analysis reported dihydrazinate of chromous chloride. A similar approach was made by Hein and Bahr[11] who reported the existence of $CrCl_2 . 3 N_2H_4$ for the product obtained by the interaction of chromous iodide and hydrazine. The studies have however remained in-complete and needed the support of physical methods particularly because chromous solution invariably contained Cr (iii) which also reacted with hydrazine. Under the circumstances, correct information about the composition of the complex could not be arrived at b merely employing the method of chemical analysis.

The present chapter deals with the electrometric (potentiometric and amperometric) studies on the composition of Cr (ii) and (iii) hydrazine complexes.

E X P E R I M E N T A L

Preparation of Chromous Chloride solution:

The method recommended by Bathis and Bailer[16] was followed with slight modifications. The solution of chromous chloride was obtained by the zinc-HCl reuction of chromic choride.

About 80 gm of A.R. granulated Zinc were mixed with 100 cc of 50% solution of chromic chloride (Anala R) and treated with 125 cc of pure distilled HCl in small quantities. The chromous chloride thus obtained was converted to chromous acetate by adding 200 cc of 75% sodium acetate maintaining an inert atmosphere of CO_2. The red precipitate of chromous acetate thus formed was kept immersed in freezing mixture and washed with ice cooled air free distilled water for several times till the filterate no more gave the test for zinc. The chromous acetate was converted to chromous chloride by dissolving the former in minimum quantity of ice cooled 1.0N HCl. The acidic chromous chloride solution thus obtained was treated with a slow and continuous stream of purified HCl gas in an inert atmosphere of nitrogen. After 2-3 hours, blue crystals of chromous chloride were appeared, these crystals were washed several times with air free ice cooled distilled water. And, finally these crystals were

dissolved in about 200 cc of air free conductivity water giving thereby a neutral solution of chromous chloride. It was stored in a stone's[17] bottle and remained stable for several months.

The method of Zintl and Rienacker[18] for the determination of the strength of chromous chloride using copper sulphate or potassium dichromate was replaced by a more quick and accurate method. The method depends on the oxidation of chromous chloride by potassium permanganate and titrating the excess of the latter against ferrous ammonium sulphate potentiometridally.

An approximate M solution of chromic chloride was prepared by dissolving 26.65 gm of A.R. product in 100 cc of double distilled water.

The solution was standardized by converting it into chromate with the help of sodium per oxide and then removing the excess of the latter by boiling the chromate solution with little $KHSO_4$ until the solution changes itself into permentant yellow. The chromate solution (converted into deep yellow by adding sulphuric acid in little quantity) was then titrated iodometrically against standard thio sulphate solution. From the strength of chromate solution, the amount of $CrCl_3$ may easily be estimated.

Hydrazine hydrate (B.D.H) was used during the experiments An approximately (M) solution of the reagent was prepared by adding 50 cc of hydrazine hydrate (density-1.07) in one litre

of air free distilled water.

For standardization of hydrazine hydrate, the method recommended by Dernbach and Mehling[19] was employed with few modifications.

To a known volume of hydrazine hydrate, an excess of potassium ferricyanide was added followed by the addition of sodium hydroxide to make the solution alkaline. The resulting solution was shaken thoroughly for five minutes and allowed to stand for ten minutes the reaction proceeds as follows.

$$N_2H_4 + 4\,K_3\,FeCy_6 \longrightarrow 4\,K_4\,FeCy_6 + 4\,H_2O + N_2 + 4\,KOH$$

To the solution was then added HCl to make it just acidic and then KI and little $Zn\,SO_4$. The small amount of the latter was added to check the reversible reaction.

$$2K_3\,FeCy_6 + 2KI \rightleftharpoons 2K_4\,FeCy_6 - I_2$$

$$2K_4FeCy_6 + 3\,Zn\,SO_4 \rightleftharpoons K_2\,Zn_3\,(FeCy_6) - 3K_2SO_4$$

The excess of ferricyanide was then titrated against sodium thio sulphate solution comparable results were obtained when hydrazine hydrate solution was estimated by the indirect iodate method.[20]

Chromous chloride - Hydrazine complex:

The composition of chromous chloride-hydrazine complex was investigated by applying amperometric and potentiometric methods.

Amperometric Studies:

Standard solutions of chromous chloride and hydrazine hydrate were prepared as described earlier. A $1x10^{-1}$% solution of gelatin was used as maximum suppressor and 1.0MKCl (A.R) was used as the supporting electrolyte.

A Lange's polarometer with a multiflex galvanometer type M.G.F2 in external circuit was used for amperometric studies. Nitrogen gas was purified after passing thorough chromous chloride and alkaline pyragallol.

In order to determine the value of applied potential to be used during amperometric measurements, the polarogram of chromous chloride was taken.

The apparatus was standardised and the increasing voltage was applied, noting the galvanometer (sensitivity 1: 10 and that of polarometer 2^{X}) deflection at each potential the mean of the maximum and minimum was taken as the correct reading.

Table 1.

1.0 cc $CrCl_2$ (4.01×10^{-1} N) + 2.0 cc gelatin (1×10^{-1} %) + 10 cc KCl (1.0M) + 7.0 cc H_2O

drop time = 3.8 cc.

Voltage applied	Current amp. 8.8×10^{-9}	Voltage applied	Current amp. 8.8×10^{-9}
0.0 Volt	- 12.0	0.75 Volt	+ 0.75
0.05 "	- 11.5	0.80 "	+ 1.5
0.10 "	- 11.5	0.85 "	+ 2.5
0.15 "	- 11.5	0.90 "	+ 4.5
0.20 "	- 11.0	0.95 "	+ 7.25
0.25 "	- 10.5	1.0 "	+ 12.5
0.30 "	- 9.0	1.05 "	+ 19.25
0.40 "	- 3.75	1.10 "	+ 26.5
0.50 "	- 0.75	1.15 "	+ 37.5
0.55 "	0	1.20 "	+ 45.75
0.60 "	0	1.25 "	+ 43.0
0.65 "	+ 0.25	1.30 "	+ 46.25
0.70 "	+ 0.25	1.35 "	+ 50.0

Fig. 1.

A graph was plotted between galvanometer deflections and the applied voltage. It extends in two parts, namely Cathodic and anodic where the oxidation of Cr^{++} to Cr^{+++} and reduction of Cr^{+++} to Cr^{++} takes place. The potential to be applied for amperometric titrations was found to be - 0.2 volts (from the platean of the polarogram).

Amperometric titrations were carried out between $CrCl_2$ (in the cell) and hydrazine hydrate. A known volume of $CrCl_2$ was taken in the cell (under inert atmosphere of nitrogen and covered with a thin layer of kerosine oil) containing base electrolyte and the maximum suppressor. The drop time (3 secs) was adjusted and a constant potential of - 0.2 volt was applied Aliquots of hydrazine hydrate were added from the microburette and readings of the galvanometer were taken after mixing of the reagents by the current of nitrogen.

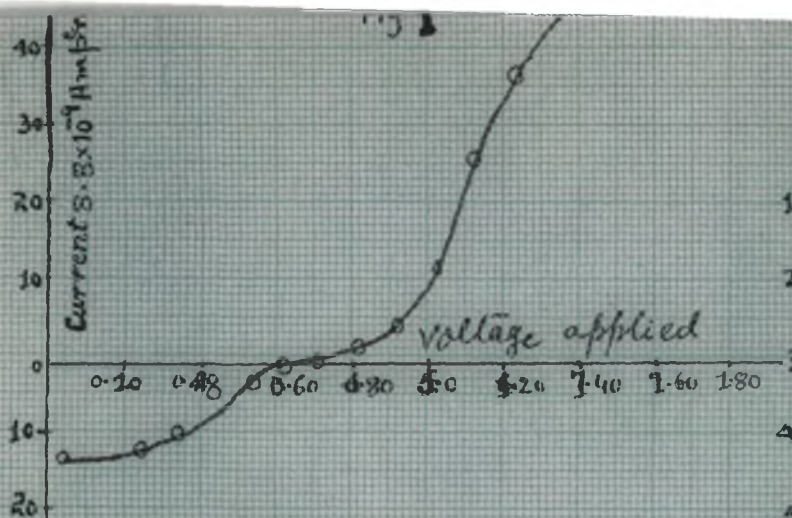
Set I. 1.0 cc of $CrCl_2$ (4.01×10^{-1}N) + 10.0 cc KCl (1M) + 2.0 cc gelatin (1×10^{-2}%) + 7.0 cc H_2O against 1.78×10^{-1}N $N_2H_4.H_2$) .

Set II. 1.0 cc of $CrCl_2$ (4.01×10^{-1}N) + 0.5 cc $CrCl_3$ (5×10^{-1}M) + 10.0 cc KCl (1M) + 2.0 cc gelatin (1×10^{-2}%) + 6.5 c H_2O against 1.95×10^{-1}N $N_2H_4 . H_2O$.

Set III. 1.0 cc of $CrCl_2$ (3.53×10^{-1}N) + 0.1 cc $CrCl_3$ (5×10^{-1}M) - 10.0 cc KCl (1M) - 2.0 cc (1×10^{-2}%) + 6.9 cc H_2O against 1.50×10^{-1}N $N_2H_4 . H_2O$.

Set IV. 1.0 cc of $CrCl_2$ (3.53×10^{-1}N) + 0.2 cc $CrCl_3$ (5×10^{-1}M) + 10.0 cc KCl (1M) + 2.0 cc gelatin (1×10^{-2}%) + 6.8 cc H_2O against 1.50×10^{-1}N $N_2H_4 . H_2O$.

Set V. 1.0 cc of $CrCl_2$ (3.53×10^{-1}N) + 10.0 cc KCl (1M) + 2.0 cc gelatin (1×10^{-2}%) + 7.0 cc H_2O against 1.50×10^{-1}N $N_2H_4 . H_2O$.



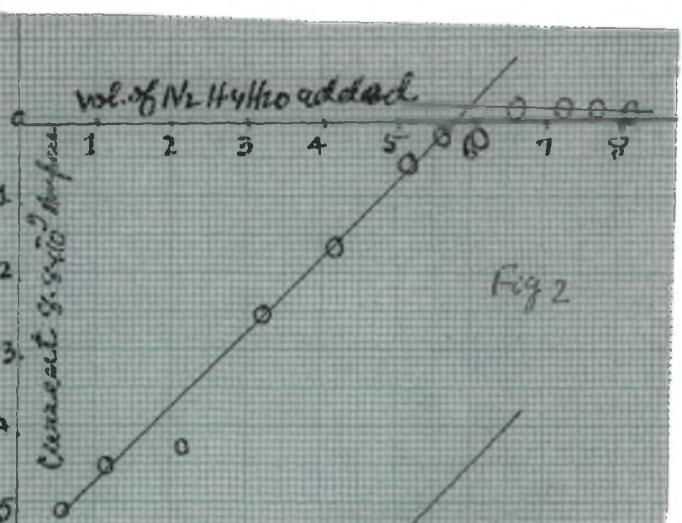


Fig 2

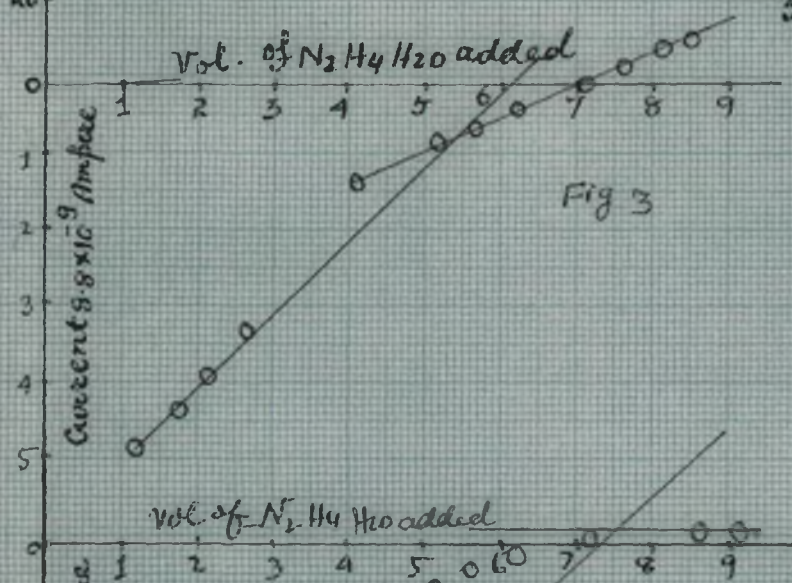


Fig 3

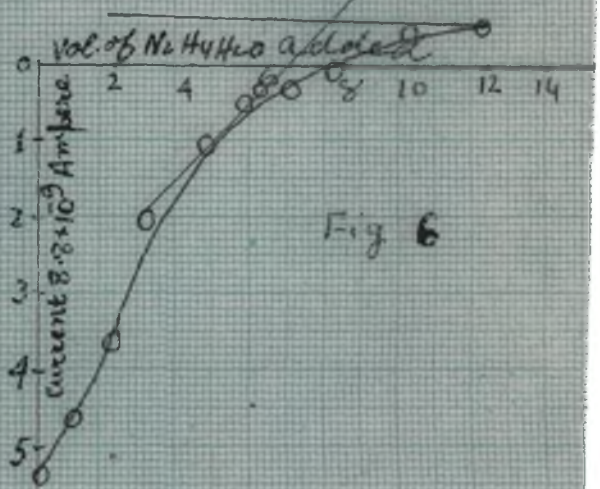


Fig 6

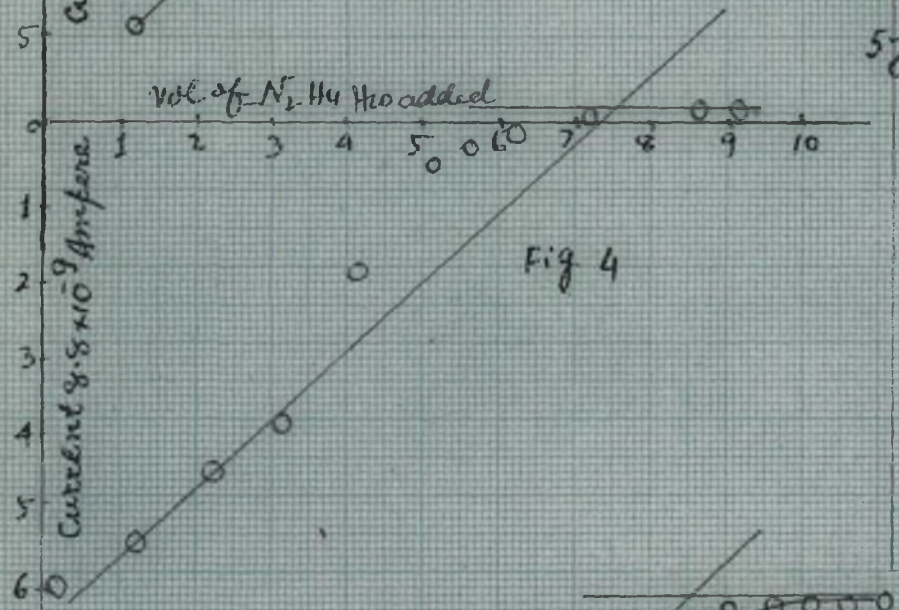


Fig 4

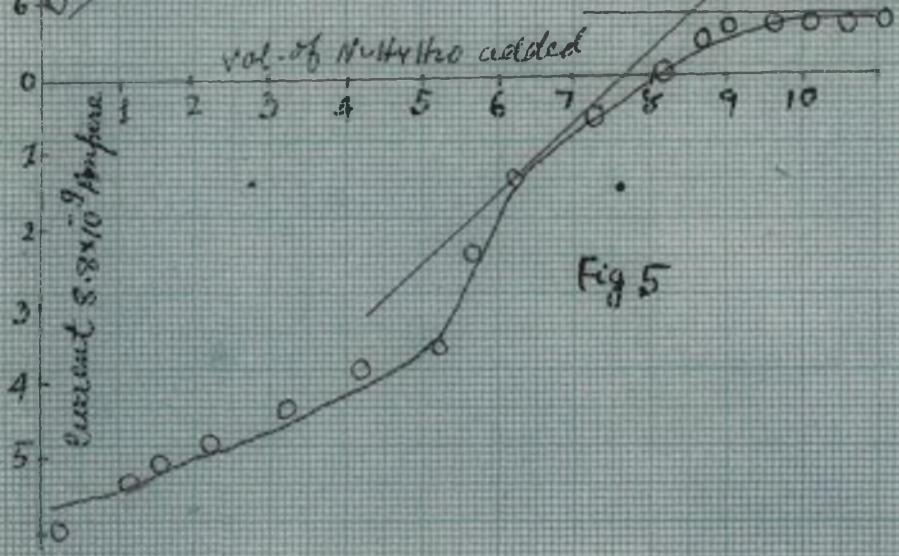


Fig 5

Table 2.

Set I		Set II		Set III	
Vol. of 1.78 $x10^{-1}$N $N_2H_4.H_2O$ (c.c's)	Current $8.8x10^{-9}$ amp.	Vol. of $1.95x10^{-1}$N $N_2H_4.H_2$) (c.c's)	Current $8.8x10^{-9}$ amp.	Vol. of $1.50x10^{-1}$N $N_2H_4.H_2O$ (c.c's)	Current $8.8x10^{-9}$ amp.
0	- 5.5	0	- 6.5	0	- 6.0
0.5	- 5.0	0.5	- 5.0	1.0	- 5.5
1.0	- 4.75	1.0	- 4.5	2.0	- 4.5
1.5	- 4.25	1.5	- 4.25	3.0	- 4.0
2.0	- 3.75	2.0	- 4.0	4.0	- 2.0
2.5	- 3.25	2.5	- 3.5	4.5	- 1.0
3.0	- 2.25	3.0	- 1.5	5.0	- 0.5
3.5	- 1.50	3.5	- 1.25	6.0	- 0.15
4.0	- 1.250	4.0	- 1.25	7.0	0
4.5	- 1.0	4.5	- 0.75	8.5	0
5.0	- 0.75	5.0	- 0.50	10.0	0
6.0	- 0.25	6.0	0	11.0	+ 0.25
7.0	0	8.0	0	12.0	+ 0.25
8.0	+ 0.50	10.0	+ 0.25		

Fig. 2. Fig. 3. Fig. 4.

i) 1.0 cc $CrCl_2$ ($4.01x10^{-1}$N) + 0 cc $CrCl_3$ ≡ 5.9 cc ($1.78x10^{-1}$N) $N_2H_4 . H_2O$.

ii) 1.0 cc $CrCl_2$ ($4.01x10^{-1}$N) + 0.5 cc $CrCl_3$ ($5x10^{-2}$M) ≡ 5.3 cc ($1.95x10^{-1}$N) $N_2H_4 . H_2O$.

iii) 1.0 cc $CrCl_2$ ($3.53x10^{-1}$N) + 0.1 cc $CrCl_3$ ($5x10^{-2}$M) ≡ 7.5 cc ($1.50x10^{-1}$N) $N_2H_4 . H_2O$.

Table 3.

Set IV.				Set V.			
Vol. of 1.50 x 10^{-1} N $N_2H_4.H_2O$ c.c's	Current 8.8×10^{-9} amp.	Vol. of 1.50 x 10^{-1} N $N_2H_4.H_2O$ c.c's	Current 8.8×10^{-9} amp.	Vol. of 1.50 x 10^{-1} N $N_2H_4.H_2O$ c.c's	Current 8.8×10^{-9} amp.	Vol. of 1.50 x 10^{-1} N $N_2H_4.H_2O$ c.c's	Current 8.8×10^{-9} amp.
0	-6.0	7.0	-0.5	0	-4.5	6.0	-0.25
1.0	-5.25	7.5	-0.25	2.0	-3.5	6.5	-0.25
2.0	-4.75	8.0	0	3.0	-2.0	7.0	-0.25
3.0	-4.25	8.5	+0.5	3.5	-2.0	8.0	0
4.0	-3.75	9.0	+0.75	4.5	-1.0	9.0	+0.25
5.0	-3.5	10.0	+0.75	5.0	-1.0	10.0	+0.25
5.5	-2.25	11.0	+0.75	5.5	-0.50	11.0	+0.25
6.0	-1.25						

Fig. 5.

Fig. 6.

iv) 1.0 cc $CrCl_2$ (3.53×10^{-1}N) + 0.2 cc $CrCl_3$ (5×10^{-1}M) ≡ 8.2 cc (1.50×10^{-1}N) $N_2H_4.H_2O$.

v) 1.0 cc $CrCl_2$ (3.53×10^{-1}N) + 0 cc $CrCl_3$ ≡ 8.0 cc (1.50×10^{-1}N) $N_2H_4.H_2O$.

Potentiometric Studies:

The potentiometric studies were carried out using a Tinsley Vernier potentiometer (Tupe 3387B) connected to a sensitive mirror galvanometer with lamp and scale arrangement. The indicator electrode consisted of the bright platinum electrode dipped in chromous chloride solution forming thereby

Fig. 7.

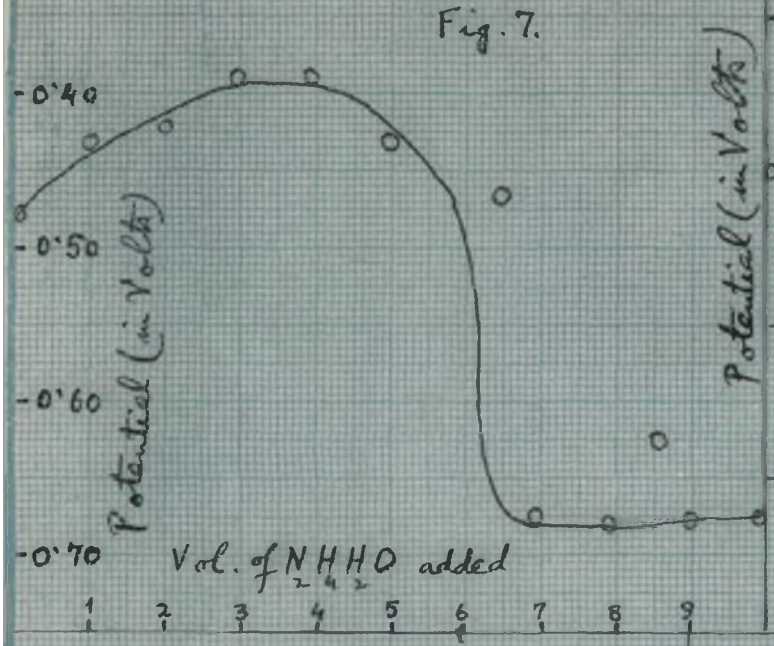


Fig. 9

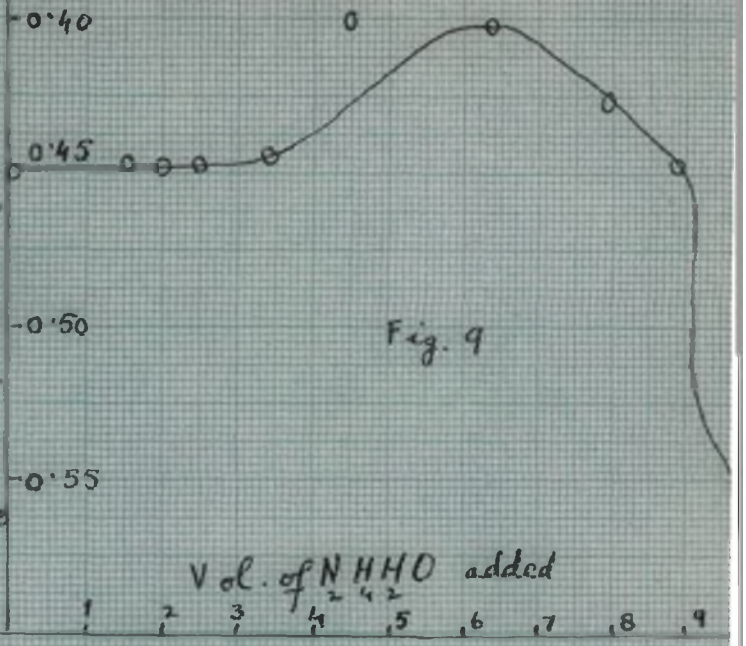


Fig. 8.

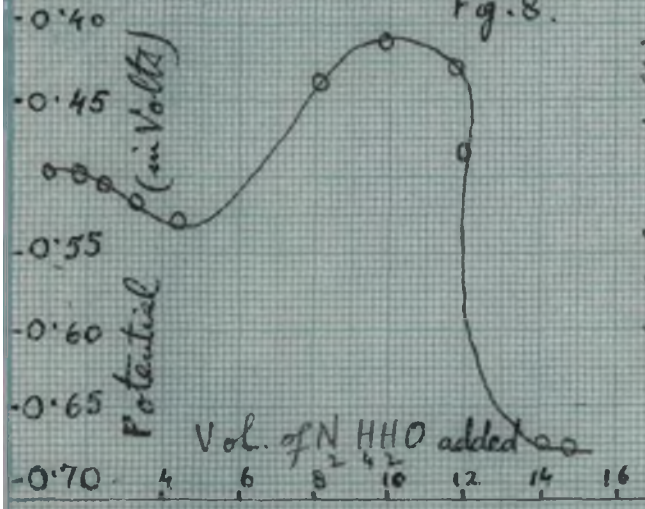


Fig. 10

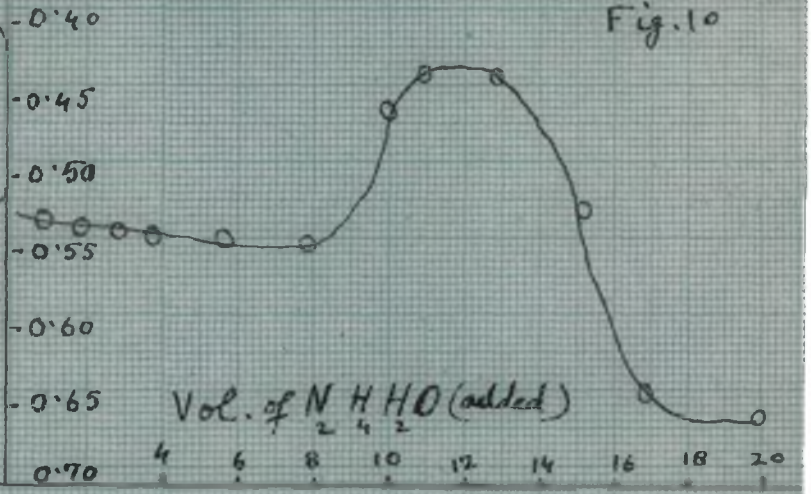
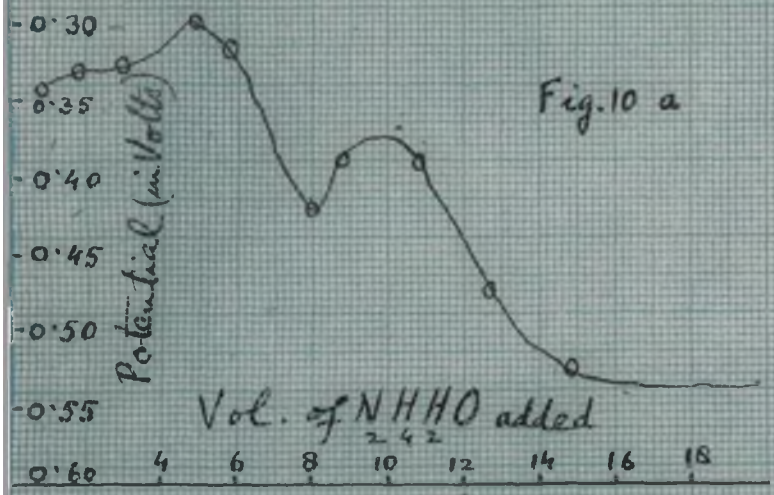


Fig. 10 a



$Cr^{++} \rightleftharpoons Cr^{+++} + e$ couple calomel electrode served as the reference electrode.

The potentiometric titrations were carried out by taking a known volume (2.0 cc) of CrCl solution in a small wide mouthed bottle with a cork carrying the electrodes and with arrangement for passing CO_2 and inserting the nozzle of the burette. Hydrazine was then added to the solution and readings were taken 5 minutes after each addition and stirring the mixture well.

Titrations were carried out with 6.84×10^{-1}M $CrCl_2$ (containing varying amounts of 1.2M $CrCl_3$) against 7.5×10^{-1}M hydrazine hydrate.

Set I.

2.0 cc $CrCl_2$ (6.84×10^{-1}M) + 8.0 cc (air free distilled water) against 7.5×10^{-1}M $N_2H_4 . H_2O$.

Set II.

2.0 cc $CrCl_2$ (6.84×10^{-1}M) + 2.0 cc $CrCl_3$ (1.2M) + 6.0 cc (air free distilled water) against 7.5×10^{-1}M $N_2H_4 . H_2O$

Set III.

2.0 cc $CrCl_2$ (6.84×10^{-1}M) + 2.0 cc $CrCl_3$ (1.2M) + 4.0 cc (air free distilled water) against 7.5×10^{-1}M $N_2H_4 . H_2O$

Set IV.

2.0 cc $CrCl_2$ (6.84×10^{-1}M) + 6.0 cc $CrCl_3$ (1.2M) + 2.0 cc (air free distilled water) against 7.5×10^{-1}M $N_2H_4 . H_2O$.

Table 4.

Set I.		Set II.		Set III.		Set IV.	
Vol.of $N_2H_4.H_2O$ c.c.'s	Potential (Volts) (Calomel-)	Vol. of $N_2H_4.H_2O$ c.c.'s	Potential (Volts) (Calomet-)	Vol.of $N_2H_4.H_2O$ c.c.'s	Potential (Volts) (Calomel-)	Vol. of $N_2H_4.H_2O$ c.c.'s	Poten-tial (Volts (Calome
0	0.494	1.0	0.482	0	0.450	0	0.5285
0.5	0.426	1.5	0.440	0.75	0.4775	0.5	0.5325
1.0	0.430	2.0	0.445	1.0	0.4845	1.0	0.5345
1.5	0.428	2.5	0.447	1.5	0.4895	2.0	0.5355
2.0	0.429	3.5	0.434	2.0	0.4940	3.0	0.5380
2.5	0.415	4.5	0.448	2.5	0.5000	4.0	0.5420
2.7	0.4165	5.5	0.418	3.5	0.5100	6.0	0.5550
3.0	0.394	6.5	0.40	4.5	0.5235	8.0	0.5530
3.2	0.3885	8.0	0.390	5.5	0.5240	10.0	0.4620
3.5	0.3875	8.5	0.40	7.5	0.4540	11.0	0.4350
4.0	0.397	9.0	0.425	8.5	0.4330	13.0	0.470
4.5	0.4275	10.0	0.450	10.0	0.4100	15.0	0.5250
5.0	0.448		0.537	11.0	0.4130	17.0	0.6350
5.5	0.465		0.594	12.0	0.4750	18.0	0.6270
6.5	0.529			13.0	0.5410		
7.5	0.620			14.0	0.670		
10.0	0.67			15.0	0.6550		

Fig. 7. Fig. 8. Fig. 9. Fig. 10.

i) 2.0 cc $CrCl_2$(6.84×10^{-1}M) $\equiv$ 6.4 cc N_2H_4 (7.5×10^{-1}M) + 0 cc $CrCl_3$.

ii) 2.0 cc $CrCl_2$(6.84×10^{-1}) $\equiv$ 12.1 cc N_2H_4 (7.5×10^{-1}M) + 2.0 cc $CrCl_3$ (1.20M).

iii) 2.0 cc $CrCl_2$(6.84×10^{-1}M) $\equiv$ 9.0 cc N_2H_4 (7.5×10^{-1}M) + 4.0 cc $CrCl_3$ (1.20M).

iv) 2.0 cc $CrCl_2$(6.84×10^{-1}M) $\equiv$ 15.5 cc N_2H_4 (7.5×10^{-1}M) + 6.0 cc $CrCl_3$ (1.20M).

Chromic Chloride - Hydrazine Complex:

Chromic chloride formed a bluish green insoluble compound with hydrazine hydrate. The composition of the complex was investigated by employing amperometric and potentiometric methods.

Amperometric Studies:

Standard solutions of chromic chloride and hydrazine hydrate were prepared as described earlier. Gelatin ($1x10^{-1}$% and KCl (1.0M) were used as maximum suppressor and supporti electrolyte respectively. The amperometric studies were carried out with Lang's polarometer with a multiflex galvanometer type M.G.F 2 in external circuit.

The value of applied potential to be used during amperometric titrations was determined by plotting an applied voltage- current curve for $CrCl_3$.

A current of purified nitrogen was passed for about 10 minutes in a polarographic cell containing 1.0 cc $CrCl_3$ ($1x10^{-1}$M), 5.0 cc KCl (2M), 2.0 cc gelatin ($1x10^{-1}$%) and 12.0 cc air free distilled water. The apparatus was standardized and the current was measured (at 2x sensitivit of the polarometer and 1:10 galvanometer sensitivity) at increasing applied voltages. Noting, the galvanometer deflection at each potential the mean of the maximum and minimum oscillations were taken as the correct readings.

The readings are recorded in the following lines.

Table 5.

1.0 cc $CrCl_3$ + 5.0 cc KCl (2M) + 2.0 cc gelatin (0.1%) + 12.0 cc water.

drop time = 3.3 secs.

Voltage applied (in Volts)	Current (8.8×10^{-9} amp.)	Voltage applied (in Volts)	Current (8.8×10^{-9} amp.)
0	- 8.0	0.90	- 3.75
0.10	- 7.0	1.00	- 0.75
0.20	- 8.0	1.10	+ 3.00
0.30	- 8.0	1.20	+ 6.50
0.40	- 8.0	1.30	+ 12.0
0.50	- 7.0	1.40	+ 29.0
0.60	- 7.0	1.50	+ 47.0
0.80	- 7.0	1.60	+ 48.0

Fig. 11.

The potential to be applied for amperometric titrations was found to be -1.20 volts(from the voltage- current curve).

Amperometric titrations between chromic chloride and hydrazine (both direct and reverse) were carried at a constant potential of - 1.20 volt.

The observations are recorded in the following lines.

Direct Titrations: Chromic chloride (in the cell) against hydrazine hydrate.

Set I.

2.0 cc $CrCl_3$ ($5x10^{-2}M$) + 2.0 cc gelatin ($1x10^{-1}$%) + 5.0 cc KCl (2M) + 11.0 cc H_2O against $2x10^{-2}M$ $N_2H_4.H_2O$.

Set II.

1.0 cc $CrCl_3$ ($2x10^{-1}M$) + 5.0 cc KCl (2M) + 2.0 cc gelatin ($1x10^{-1}$%) + 12.0 cc H_2O against $5x10^{-2}M$ $N_2H_4.H_2O$.

Set III.

4.0 cc $CrCl_3$ ($5x10^{-2}M$) + 2.0 cc gelatin ($1x10^{-1}$%) + 5.0 cc KCl (2M) + 10.0 cc H_2O against $6.6x10^{-2}M$ $N_2H_4.H_2O$.

Table 6.

Voltage applied:- 0.120 volt.

Set I.		Set II.		Set III.	
Vol. of $N_2H_4.H_2O$ ($2x10^{-2}M$) (c.c's)	Current $8.8x10^{-9}$ amp.	Vol. of $N_2H_4.H_2O$ ($5x10^{-2}M$) (c.c's)	Current $8.8x10^{-9}$ amp.	Vol. of $N_2H_4.H_2O$ ($6.6x10^{-2}M$) (c.c's)	Current $8.8x10^{-8}$ amp.
0	40.5	0	82	0	10.40
0.10	44.0	0.10	95	0.20	11.00
0.30	45.0	0.40	84.5	0.40	12.50
0.60	39.5	0.70	45	0.60	12.80
0.80	25.0	1.00	23.5	1.00	6.45
1.00	14.0	1.50	24.5	1.20	3.90
1.50	11.5	2.00	22.0	1.50	2.30
1.70	8.0	4.00	18.5	2.00	1.60
2.00	7.5	6.00	4.5	2.50	1.40
2.50	5.5	8.00	2.5	3.00	0.60
3.50	5.5			4.00	0.30
5.00	5.5				
10.00	5.5				

Fig. 12. Fig. 13. Fig. 14.

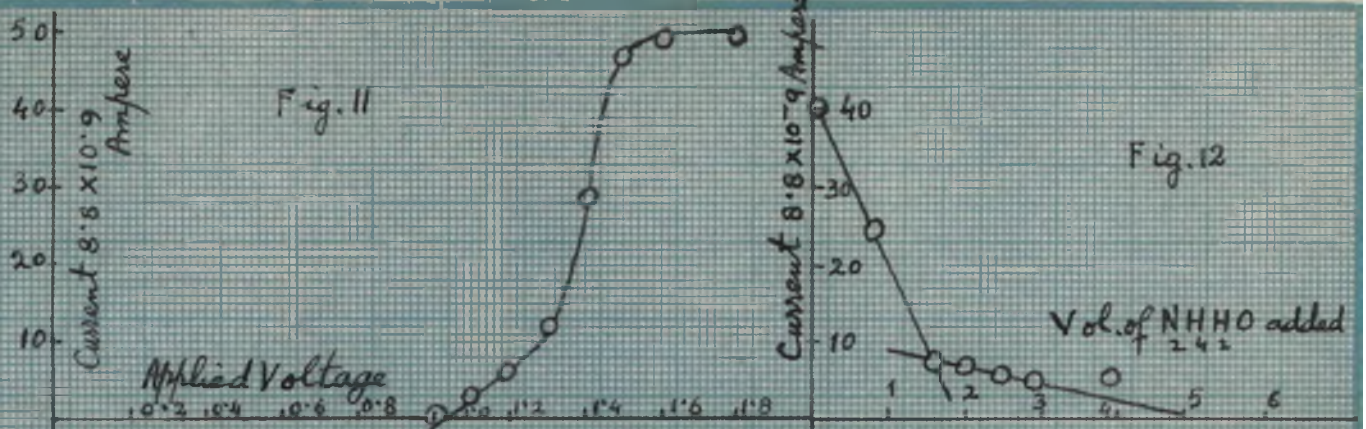


Fig. 11

Fig. 12

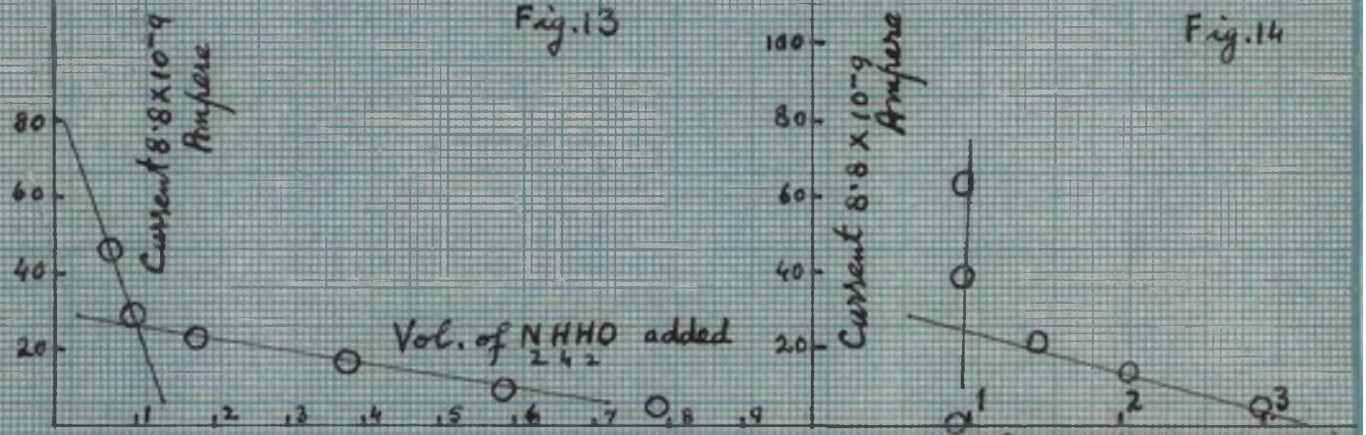


Fig. 13

Fig. 14

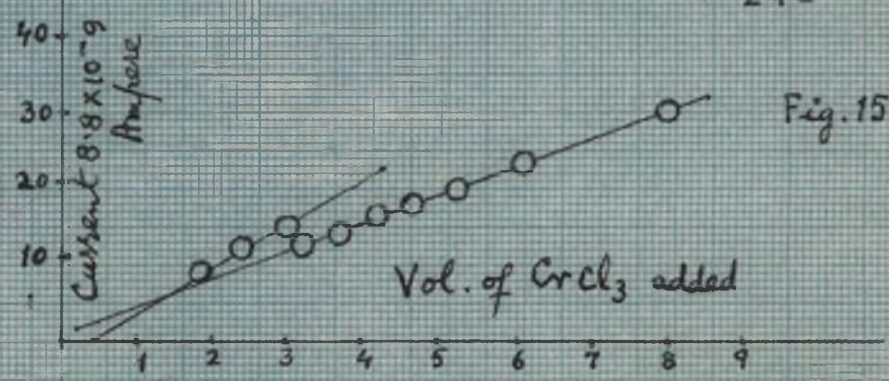


Fig. 15

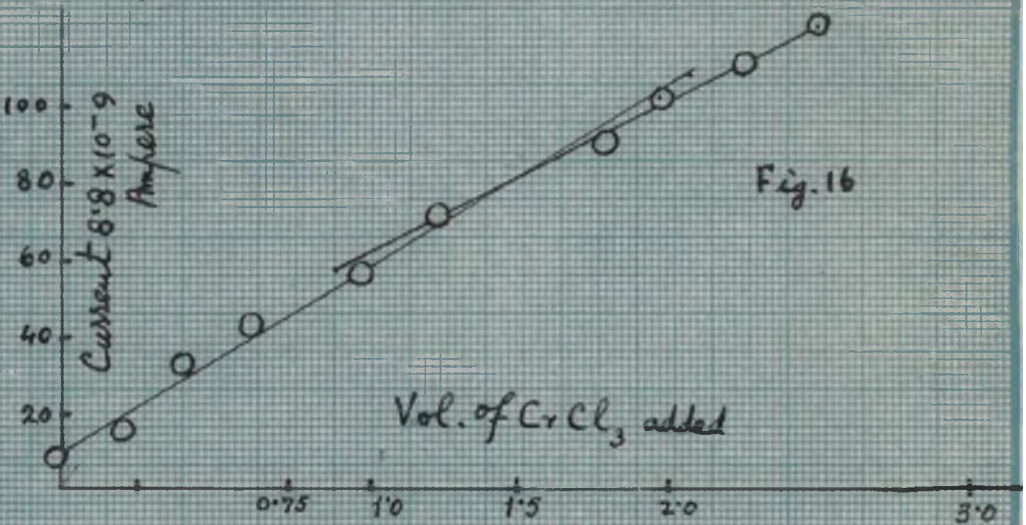


Fig. 16

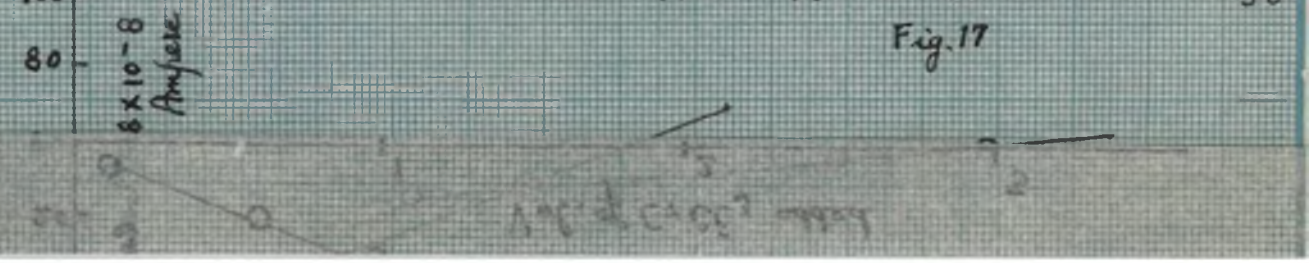


Fig. 17

i) 2 cc $CrCl_3$ ($5x10^{-2}$M) ≡ 1.7 cc $N_2H_4.H_2O$ ($2x10^{-2}$M)

ii) 1.0 cc $CrCl_3$($2x10^{-1}$M) ≡ 1.2 cc $N_2H_4.H_2O$ ($5x10^{-2}$M)

iii) 4.0 cc $CrCl_3$ ($5x10^{-2}$M) ≡ 1.0 cc $N_2H_4.H_2O$ ($6.6x10^{-2}$M)

Reverse Titrations: Hydrazine hydrate (in the cell) against chromic chloride.

Set I. 1.0 cc $N_2H_4.H_2O$ ($1x10^{-1}$M) + 4.0 cc KCl (2M) + 2.0 cc gelatin ($1x10^{-1}$%) + 13.0 cc H_2O gainst $2x10^{-1}$M $CrCl_3$.

Set II. 3.0 cc $N_2H_4.H_2O$ ($5x10^{-2}$M) + 4.0 cc KCl (2M) + 2.0 cc gelatin ($1x10^{-1}$%) + 11.0 cc H_2O against $3.3x10^{-1}$M $CrCl_3$.

Set III. 4.0 cc $N_2H_4.H_2O$ ($2.5x10^{-2}$M) + 4.0 cc KCl (2M) + 2.0 cc gelatin ($1x10^{-1}$%) + 10.0 cc H_2O against $2x10^{-1}$M $CrCl_3$.

Table 7.

Voltage applied:- 1.20 volt.

Set I.		Set II.		Set III.	
Vol. of $CrCl_3$ 6 H_2O ($2x10^{-1}$M) (c.c's)	Current $8.8x10^{-9}$ amp.	Vol. of $CrCl_3$ 6 H_2O ($3.3x10^{-1}$M) (c.c's)	Current $8.8x10^{-9}$ amp.	Vol. of $CrCl_3$ 6 H_2O ($2x10^{-1}$M) (c.c's)	Current $8.8x10^{-8}$ amp.
0	0.5	0	0.30	0	1.0
0.30	1.75	0.20	1.25	0.1	0.80
0.80	2.0	0.40	3.10	0.6	2.00
1.80	8.0	0.60	4.25	1.0	3.10
2.30	9.75	0.80	5.00	1.2	4.50
3.10	12.25	1.00	5.35	1.5	5.00
3.60	14.0	1.10	6.35	1.8	4.50
4.10	16.0	1.30	7.50	2.5	5.50
4.60	18.0	1.80	9.00	3.5	9.00
5.10	19.5	2.00	10.00	5.0	11.25
6.00	23.0	3.00	13.50		
8.00	30.0	5.00	13.80		
10.00	36.5	6.00	24.00		
15.00	53.0	8.00	34.20		

Fig. 15. Fig. 16. Fig. 17.

i) 1.35 cc $CrCl_3$ ($2x10^{-1}M$) $\equiv$ 1.0 cc $N_2H_4 . H_2O$ ($1x10^{-1}M$)

ii) 1.45 cc $CrCl_3$ ($3.3x10^{-1}M$) $\equiv$ 3.0 cc $N_2H_4 . H_2O$ ($5x10^{-2}M$)

iii) 1.45 cc $CrCl_3$ ($2x10^{-1}M$) $\equiv$ 4.0 cc $N_2H_4 . H_2O$ ($2.5x10^{-2}M$)

Potentiometric Studies:

The potentiometric titrations were carried out, using a Tinsley Vernier potentiometer (Type 3387B) connected to sensitive mirror galvanometer with lamp scale arrangement. The electrodes employed were, bright platirum indicator elect rode and calomel electrode served as reference electrode. The vessel used for titrations was of the same type as used in case of chromous-hydrazine complex. Both reverse and direct titrations were carried out between chromic chloride and hydrazine.

Direct Titrations: Chromic chloride (in the cell) against hydrazine hydrate.

Set I.

10.0 cc of $CrCl_3 6 H_2O$ ($2x10^{-1}M$) against $3.3x10^{-1}M$ $N_2H_4 . H_2O$.

Set II.

10.0 cc of $CrCl_3 6 H_2O$ ($1x10^{-1}M$) against $3.3x10^{-1}M$ $N_2H_4 . H_2O$.

Set III.

10.0 cc of $CrCl_3 6 H_2O$ ($5x10^{-2}M$) against $1x10^{-1}M$ $N_2H_4 . H_2O$.

Table 8.

Set I.		Set II.		Set III.	
Vol. of $N_2H_4.H_2O$ (3.3×10^{-1} M)	Potential (Volts) (Calomel-)	Vol. of $N_2H_4.H_2O$ (3.3×10^{-1} M)	Potential (Volts) (Calomel-)	Vol. of $N_2H_4.H_2O$ (1×10^{-1} M)	Potential (Volts) (Calomel-)
c.c's		c.c's		c.c's	
0	0.35	0	0.148	0	0.026
0.2	0.42	0.5	0.150	0.5	0.081
0.7	0.44	1.0	0.161	0.7	0.088
2.0	0.355	1.2	0.163	1.0	0.092
2.5	-0.11	1.5	0.168	1.5	0.10
3.0	(Calomel-)		0.176	2.0	0.110
3.5	0.3	1.9	0.177	3.0	0.130
4.0	0.81	2.0	0.179	4.0	0.188
4.5	0.155	2.5	0.185	5.0	0.190
5.5	0.160	3.0	0.189	7.0	0.194
6.5	0.164	3.5	0.190		
8.5	0.169	5.0	0.196		
	0.180	7.0			

Fig. 18 Fig. 19 Fig. 20.

i) 10.0 cc $CrCl_3$ (2×10^{-1} M) $\equiv$ 2.3 cc $N_2H_4.H_2O$ (3.3×10^{-1} M)

ii) 10.0 cc $CrCl_3$ ($1\times10^{-}$ M) $\equiv$ 1.1 cc $N_2H_4.H_2O$ (3.3×10^{-1} M)

iii) 10.0 cc $CrCl_3$ (5×10^{-2} M) $\equiv$ 2.0 cc $N_2H_4.H_2O$ (1×10^{-1} M)

Reverse Titrations: Hydrazine hydrate (in the cell) against chromic chloride.

Set I. 10.0 cc $N_2H_4.H_2O$ (1×10^{-1} M) against $CrCl_3 6H_2O$ (2.5×10^{-1} M).

Set II. 10.0 cc $N_2H_4.H_2O$ (2×10^{-1} M) against $CrCl_3 6H_2O$ (6.66×10^{-1} M).

Set III. 10.0 cc $N_2H_4.H_2O$ (5×10^{-2} M) against $CrCl_3 6H_2O$ (1.66×10^{-1} M).

Table 9.

Set I.		Set II.		Set III.	
Vol. of $CrCl_3$ 6 H_2O (c.c's)	Potential (Volts) (Calomel+)	Vol. of $CrCl_3$ 6 H_2O (c.c's)	Potential (Volts) (Calomel+)	Vol. of $CrCl_3$ 6 H_2O (c.c's)	Potential (Volts) (Calomel+)
		0			
0	0.305	5.0	0.318	0	0.295
0.50	0.220	7.0	0.270	2.0	0.205
0.70	0.202	10.0	0.250	5.0	0.178
10.0	0.195	15.0	0.243	10.0	0.170
12.0	0.188	20.0	0.213	15.0	0.152
15.0	0.186	25.0	0.203	20.0	0.209
20.0	0.157	27.0	0.201	30.0	0.170
25.0	0.132	30.0	0.18	40.0	0.207
30.0	0.165		0.178	50.0	0.211
35.0	0.165				
45.0	0.210				
50.0	0.210				

Fig. 21. Fig. 22. Fig. 23.

i) 11.0 cc 2.5 $x10^{-1}$M $CrCl_3$ $\equiv$ 10.0 cc $N_2H_4 . H_2O$ ($1x10^{-1}$M)

ii) 8.5 cc $6.66x10^{-1}$M $CrCl_3$ $\equiv$ 10.0 cc $N_2H_4 . H_2O$ ($2x10^{-1}$M)

iii) 9.0 cc $1.66x10^{-1}$M $CrCl_3$ $\equiv$ 10.0 cc $N_2H_4 . H_2O$ ($5x10^{-2}$M)

Direct Titrations: Chromic chloride (in the cell) against hydrazine hydrate.

Set I. 10.0 cc $CrCl_3$ 6 H_2O ($2x10^{-1}M$) against $3.3x10^{-1}M$ $N_2H_4 . H_2O$.

Set II. 10.0 cc $CrCl_3$ 6 H_2O ($1x10^{-1}M$) against $3.3x10^{-1}M$ $N_2H_4 . H_2O$.

Set III. 10.0 cc $CrCl_3$ 6 H_2O ($5x10^{-2}M$) against $1x10^{-1}M$ $N_2H_4 . H_2O$.

Table 10.

Set I.		Set II.		Set III.	
Vol. of $N_2H_4.H_2O$ ($3.3x10^{-1}M$) (c.c's)	Potential (Volts) (Calomel+) ve	Vol. of $N_2H_4.H_2O$ ($3.3x10^{-1}M$) (c.c's)	Potential (Volts) (Calomel+) ve	Vol. of $N_2H_4.H_2O$ ($1x10^{-1}M$) (c.c's)	Potential (Volts) (Calomel+) ve
0	0.35	0	0.148	0	0.026
0.2	0.42	0.50	0.150	0.5	0.081
0.7	0.44	1.0	0.161	0.7	0.088
2.0	0.355	1.20	0.163	1.0	0.092
2.5	0.11 (Calomel-) ve	1.50	0.168	1.5	0.10
3.0	0.30	1.90	0.176	2.0	0.110
3.5	0.81	2.0	0.177	3.0	0.130
4.0	0.155	2.50	0.179	4.0	0.188
4.5	0.160	3.0	0.185	5.0	0.190
5.5	0.164	3.50	0.189	7.0	0.194
6.5	0.164	5.0	0.190		
8.5	0.180	7.0	0.196		

Fig. 18. Fig. 19. Fig. 20.

i) 10.0 cc $CrCl_3$ ($2x10^{-1}M$) $\equiv$ 2.3 cc $N_2H_4 . H_2O$ ($3.3x10^{-1}M$)

ii) 10.0 cc $CrCl_3$ ($1x10^{-1}M$) $\equiv$ 1.1 cc $N_2H_4 . H_2O$ ($3.3x10^{-1}M$)

iii) 10.0 cc $CrCl_3$ ($5x10^{-2}M$) $\equiv$ 2.0 cc $N_2H_4 . H_2O$ ($1x10^{-1}M$)

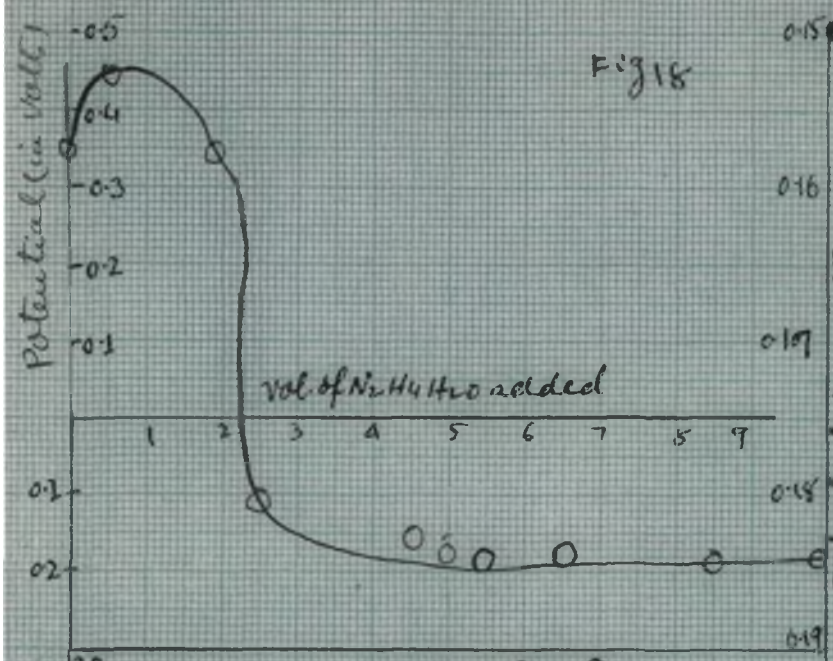


Fig 18

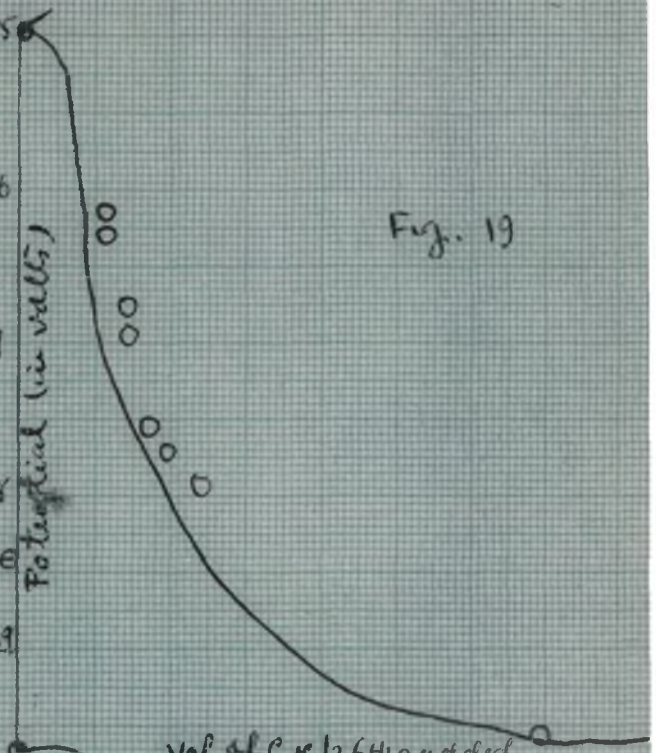


Fig. 19

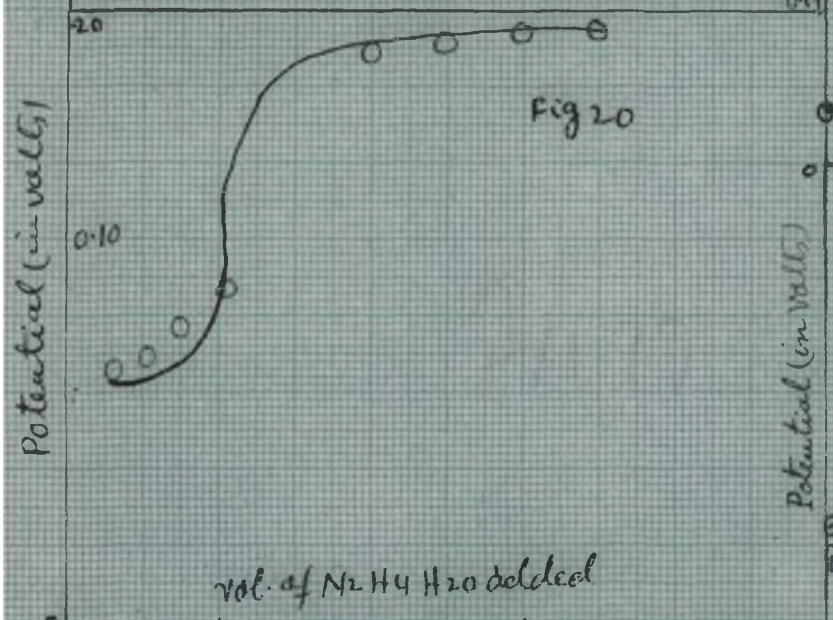


Fig 20

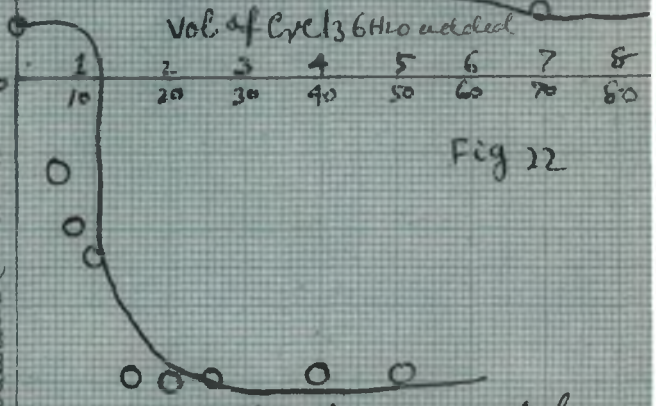


Fig 22

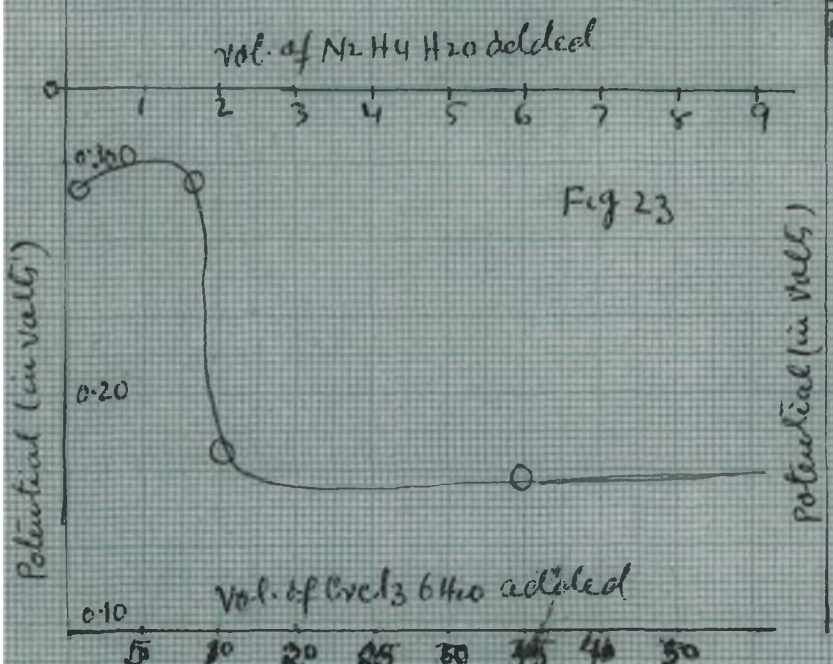


Fig 23

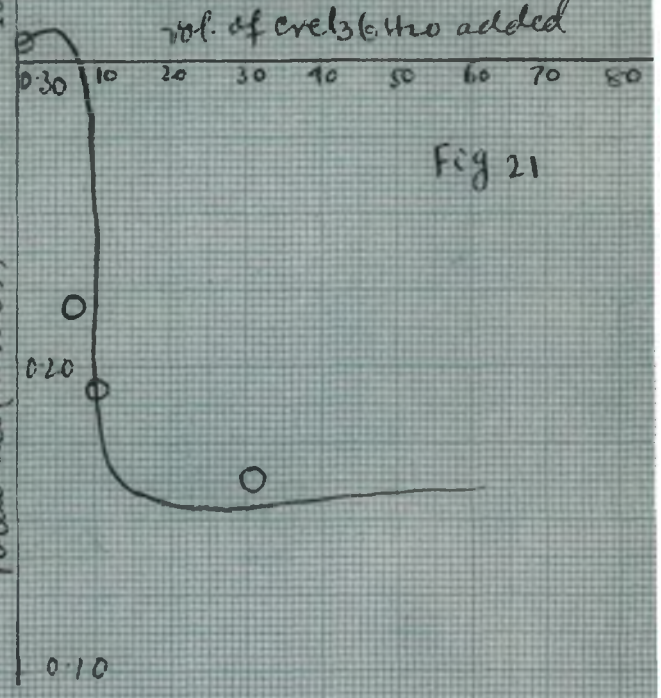


Fig 21

Reverse Titrations: Hydrazine hydrate (in the cell) against chromic chloride.

Set I. 10.0 cc $N_2H_4 . H_2O$ ($1x10^{-1}M$) against $CrCl_3$ 6 H_2O ($2.5x10^{-1}M$).

Set II. 10.0 cc $N_2H_4 . H_2O$ ($2x10^{-1}M$) against $CrCl_3$ 6 H_2O ($6.66x10^{-1}M$).

Set III. 10.0 cc $N_2H_4 . H_2O$ ($5x10^{-2}M$) against $CrCl_3$ 6 H_2O ($1.66x10^{-1}M$).

Table 11.

Vol. of $CrCl_3$ 6 H_2O ($2.5x10^{-1}M$) (c.c's)	Potential (Volt)	Vol. of $CrCl_3$ 6 H_2O ($6.66x10^{-1}M$) (c.c's)	Potential (Volt)	Vol. of $CrCl_3$ 6 H_2O ($1.66x10^{-1}M$) (c.c's)	Potential (Volt)
0	0.305	0	0.318	0	0.295
5.0	0.220	5.0	0.270	2.0	0.205
7.0	0.202	7.0	0.250	5.0	0.178
10.0	0.195	10.0	0.243	10.0	0.170
12.0	0.188	15.0	0.213	15.0	0.152
15.0	0.186	20.0	0.203	20.0	0.209
20.0	0.157	25.0	0.201	39.0	0.170
25.0	0.132	27.0	0.180	40.0	0.207
30.0	0.165	30.0	0.178	50.0	0.211
35.0	0.165				
45.0	0.210				
50.0	0.210				

Fig. 21. Fig. 22. Fig. 23.

i) 11.0 cc $2.5x10^{-1}M$ $CrCl_3$ ≡ 10.0 cc $N_2H_4 . H_2O$ ($1x10^{-1}M$)

ii) 8.5 cc $6.66x10^{-1}M$ $CrCl_3$ ≡ 10.0 cc $N_2H_4 . H_2O$ ($2x10^{-1}M$)

iii) 9.0 cc $1.66x10^{-1}M$ $CrCl_3$ ≡ 10.0 cc $N_2H_4 . H_2O$ ($5x10^{-2}M$)

D I S C U S S I O N

Chromous chloride - Hydrazine complex:

The amperometric titrations carried out between chromous chloride and hydrazine hydrate at - 0.20 volt gave the combining ratio of $CrCl_2$ to N_2H_4 as 1:3 showing thereby the existence of the complex $CrCl_2$ 3 N_2H_4. The method is trustworthy since at this potential Cr^{+++}, which also reacts with hydrazine, would not give variations in the current values by the addition of titrants.

The results are summarised in the following table.

Table 12.

Fig. No.	Solution	Vol. of $N_2H_4.H_2O$ from the curve	Strength of $CrCl_2$ in the mixture	Strength of $N_2H_4.H_2O$	Approx. Molar ratio $CrCl_2$. N_2H_4.
2	1.0 cc $CrCl_2$(4.01×10^{-1}N) + 10.0 cc KCl(1M) + 2.0cc gelatin (1×10^{-2}%) + 7.0cc H_2O.	5.9 cc	2.0×10^{-2}N	1.78×10^{-1}N	1: 2.6
3	1.0cc $CrCl_2$(4.01×10^{-1}N) + 10.0 cc KCl(1M) + 2.0 cc gelatin (1×10^{-2}%) + 0.5 cc $CrCl_3$ (5×10^{-1}M) + 6.5 cc H_2O.	5.3 cc	2.0×10^{-2}N	1.95×10^{-1}N	1: 2.6
4	1.0 cc $CrCl_2$(3.53×10^{-1}N) + 10.0 cc KCl(1M) + 2.0cc gelatin (1×10^{-2}%)+ 0.1 cc $CrCl_3$(5×10^{-1}M)+ 6.9cc H_2O	7.5 cc	1.765×10^{-1}N	1.50×10^{-1}N	1: 3.1
5	1.0 cc $CrCl_2$(3.53×10^{-1}N) + 10.0 cc KCl(1M)+ 2.0cc gelatin(1×10^{-2}%) + 0.2 cc $CrCl_3$(5×10^{-1}M)+ 6.8 cc H_2O	8.2 cc	1.765×10^{-1}N	1.50×10^{-1}N	1: 3.4
6	1.0 cc $CrCl_2$(3.53×10^{-1}N)+ 10.0 cc KCl(1M)+ 2.0cc gelatin (1×10^{-2}%) + 7.0 cc H_2O.	8.0 cc	1.765×10^{-1}N	1.50×10^{-1}N	1: 3.3

The results are furthur confirmed by potentiometric studies. This method was utilized by taking advantage of the use of Cr (ii) $\rightleftharpoons$ Cr (iii) + e couple at the bright platinum electrode. The results are summed up in the following table.

Table 13.

Fig.No.	Vol. of 6.84x 10^{-1} N $CrCl_2$	Vol. of 7.5x 10^{-1} N $N_2H_4.H_2O$	Vol. of 1.2M $CrCl_3$	Strength of $CrCl_3$ in the $CrCl_2$ sample	Vol.of $N_2H_4.H_2O$ equivalent to total $CrCl_3$	Vol.of $N_2H_4.H_2O$ reacted with $CrCl_2$	Vol.of $N_2H_4.H_2O$ of the same strength as of $CrCl_2$	Molar ratio Cr : N_2H_4
7.	2.0 cc	6.8 cc	0	0.1N	0.26 cc	6.54	7.21	1:3.6
8.	2.0 cc	9.0 cc	2.0 cc	0.1N	3.46 cc	5.54	6.08	1:3.04
9.	2.0 cc	12.1 cc	4.0 cc	0.1N	6.76 cc	5.34	5.86	1:2.93
10.	2.0 cc	15.5 cc	6.0 cc	0.1N	9.96 cc	5.54	6.08	1:3.04

These investigation do not confirm the results of Tranbe and Passarge[15], who found the existence of the complex $CrCl_2$ $2N_2H_4$. On the other hand, the composition of the complex is similar to that of chromous iodide hydrazine complex reported by Hein and Bahr. Another discrepancy observed is in the colour of the complex. While Tranbe and Passarge[15] reported the colour of the complex as red but actually the complex was isolated

as a bluish violet product. It is quite likely that some free acetate ions might be present in their solution in whose presence a red coloured compound is formed.

Chromic Chloride- Hydrazine Complex:

The amperometric studies carried out to investigate the composition of chromic chloride and hydrazine complex at - 1.20 volts gave a combining ratio of 3:1 for Cr (iii) and hydrazine respectively. The results are tabulated as follows.

Table 14.

Direct titrations: $CrCl_3 6\ H_2O$ (in the cell).

Fig.No.	Vol. of $N_2H_4.H_2O$ (from the curve)	Strength of $CrCl_3$ in the mixture	Strength of $N_2H_4.\ H_2O$	Molar ratio $CrCl_3$: N_2H_4
12.	1.7 cc	$5.0x10^{-3}M$	$2.0x10^{-2}M$	2.8: 1
13.	1.2 cc	$1.0x10^{-2}M$	$5.0x10^{-2}M$	3.3: 1
14.	1.0 cc	$10x10^{-2}M$	$6.66x10^{-2}M$	3.0: 1

Reverse Titrations: $N_2H_4 . H_2O$ (in the cell)

Fig.No.	Vol. of $CrCl_3 6H_2O$ (from the curve)	Strength of $N_2H_4 . H_2O$ in the mixture	Strength of $CrCl_3 6 H_2O$	$CrCl_3$: N_2H_4
15.	1.35	5.0×10^{-3} M	2.0×10^{-1} M	2.7: 1
16.	1.45	7.5×10^{-3} M	3.3×10^{-1} M	3.2: 1
17.	1.45	5.0×10^{-3} M	2.0×10^{-1} M	2.9: 1

More conclusive information regarding the composition of chromic chloride complex obtained from the results of potentiometry. The potentiometric measurements were carried out by using platinum indicator electrode dipped in chromic chloride solution assuming thereby the formation of $Cr^{+++} + e \rightleftharpoons Cr^{++}$ couple, calomel electrode served as the reference electrode. The containing ratio of chromic chloride and hydrazine came out to be 3:1 respectively, indicating thereby the formation of $3CrCl_3\ N_2H_4$. The results are tabulated as follows.

Table 15.

Direct Titrations: $CrCl_3 6 H_2O$ (in the cell).

Fig.No.	Vol. of $N_2H_4.H_2O$ (from the curve)	Strength of $CrCl_3$ in the mixture	Strength of $N_2H_4.H_2O$	Molar ratio $CrCl_3 : N_2H_4$
18.	2.3 cc	$2x10^{-1}M$	$3.3x10^{-1}M$	2.6: 1
19.	1.1 cc	$1x10^{-1}M$	$3.3x10^{-1}M$	2.7: 1
20.	2.0 cc	$5x10^{-2}M$	$1.0x10^{-1}M$	2.5: 1

Reverse Titrations: $N_2H_4.H_2O$ (in the cell).

Fig.No.	Vol. of $CrCl_3 6H_2O$ (from the curve)	Strength of $N_2H_4.H_2O$ in the mixture	Strength of $CrCl_3 6 H_2O$	Molar ratio $CrCl_3 : N_2H_4$
21.	11.0 cc	$1x10^{-1}M$	$2.5x10^{-1}M$	3.15: 1
22.	8.5 cc	$2x10^{-1}M$	$6.66x10^{-1}M$	2.99: 1
23.	9.0 cc	$5x10^{-2}M$	$1.66x10^{-1}M$	2.88: 1

From the foregoing studies on the chromic chloride and hydrazine complex, the formation of a complex $3CrCl_3 N_2H_4$ has been established. However, the real nature of the complex and the bonding may only be under-stood by employing chemical methods of analysis and magnetic measurements.

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C H A P T E R VI.

Bromo Complexes of Cu (i).

BROMO COMPLEXES OF Cu(i)

Amongst the halogen complexes of Cu(i) the most extensively studied are those of cuprous chloride with potassium chloride and hydro chloric acid. These have been investigated by a number of workers including Bodlander and Storback[1], Remy and Labes[2], Szabo and Szabo[3], O.A. Chaltkyan[4] and more recently by Harris[5] and Malik etal.[6] The latter authors developed a new method for determining the complex ion formation in the solid as we aqueous phase by representing the solubility data in the rectilinear phase diagram. However, retively, small amount of work has been done on bromo complexes of Cu(i). Only some old references are available amongst these worthmentioning are those of Wells and Hurlburt[7] and Fleurent.[8]

This chapter deals with the studies on the systems CuBr-KBr-H_2O, CuBr-HBr-H_2O and CuBr-Mg Br_2-H_2O at 20°C and 50°C respectively, employing besides chemical analysis, potentiometric and conductometric methods. The results are interpreted by representing solubility data in the rectilinear as well as triangular phase diagrams.[9]

E X P E R I M E N T A L

Cuprous bromide was prepared[10] by treating a mixture of copper sulphate (20 gms.) and sodium bromide (8 gms) dissolved in 300 cc of distilled water with a stream of sulphur di oxide. The white crystals so formed were washed with sulphurous acid and alcohol and finally dried with ether and kept in vacuum desiccator over caustic potash. The resulting crystals were palegreenish yellow in colour.

Cuprous ions were estimated[11] by titrating the solutions against standard thiocyanate using ferric alum as indicator.

KBr (E. Merck) was, recrystallised and used in the experiments, potassium was estimated as di potassium mono sodium cobaltinitrite.

HBr (E. Merck) was distilled and employed for the experiments, it was estimated volumetrically against standard caustic soda solution.

$MgBr_2$(Riedel) was recrystallised, dried at 110°C and estimated as magnesium ammonium phosphate hexa hydrate.

In all the experiments an excess of CuBr was dissolved in aqueous bromide solutions. The supernant liquid containing CuBr in XBr (in equilibrium with double

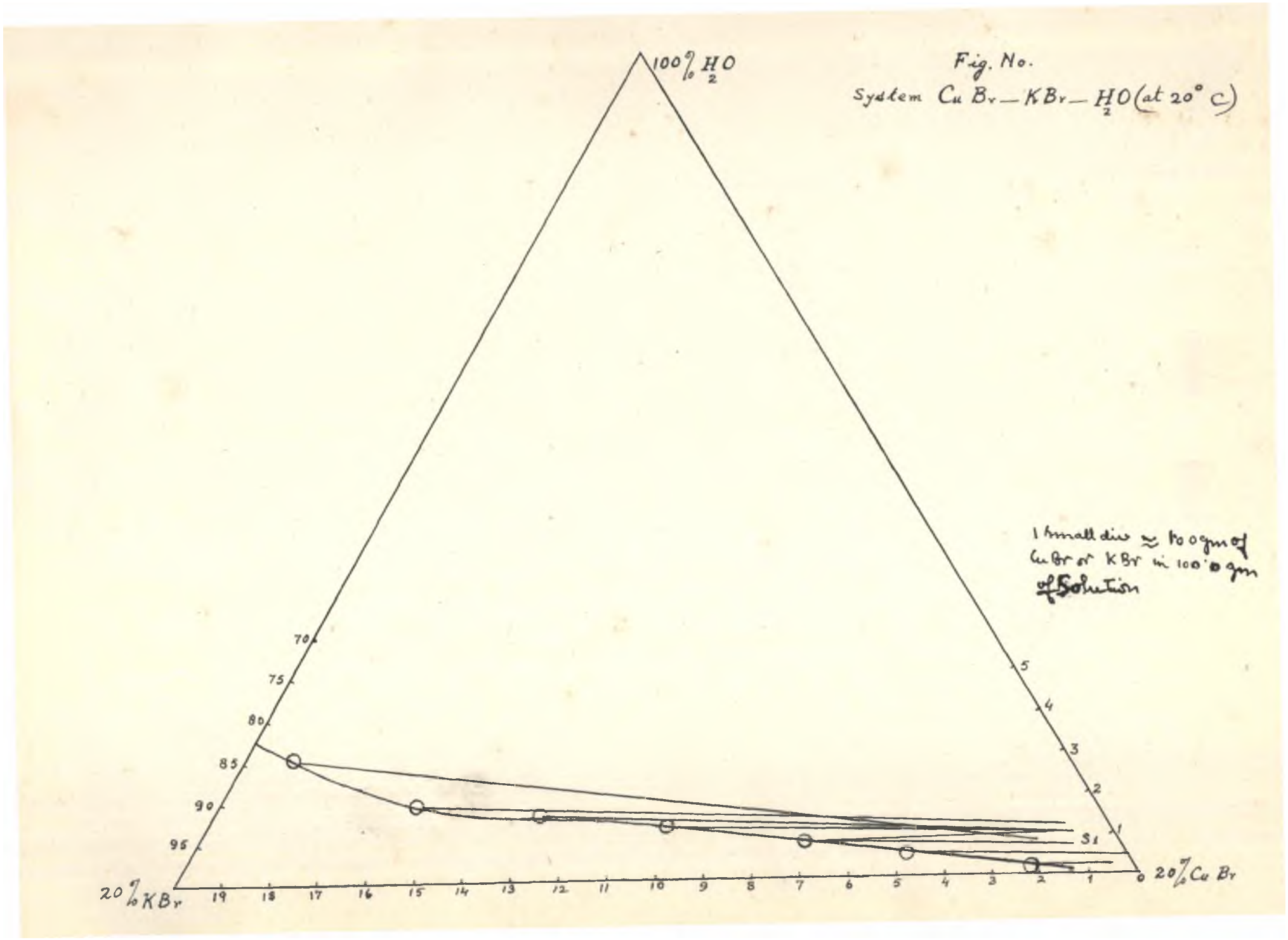


Fig. No.
System Cu Br — KBr — H_2O (at 20° C)
100% H_2O
20% KBr
20% Cu Br
1 small div ≃ 10 0 gm of Cu Br or K Br in 100·0 gm of Solution
70
75
80
85
90
95
19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
5 4 3 2 1
S1

salt CuBr. XBr) and water were mixed in the following order:

Boiling tube No. 1. 0 cc water + 40 cc solution (CuBr saturated in XBr) CuBr - XBr - H_2O (where X = H,K) at 50°C.

Boiling tube No. 2. 2 cc water + 38 cc solution

Boiling tube No. 3. 4 cc water + 36 cc solution

- - - - - - - - - - - - - - - - - -

Boiling tube No.20. 38 cc water + 2 cc solution

CuBr - XBr - H_2O at 20°C (X = Mg, K)

Boiling tube No. 1. 4 cc water + 36 cc solution

Boiling tube No. 2. 8 cc water + 32 cc solution

- - - - - - - - - - - - - - - - - -

- - - - - - - - - - - - - - - - - -

Boiling tube No. 10 36 cc water + 4 cc solution

The concentration of solid phase in equilibrium with adhering mother liquor (wet residue) was obtained by subtracting the concentration of CuBr and XBr (determined from the analysis) from the concentrations of CuBr and XBr (had it not been precipitated by adding water). The results are given in the following paragraphs, the ratios of the components from which complex formation could be approximately determined have been marked with asterisk.

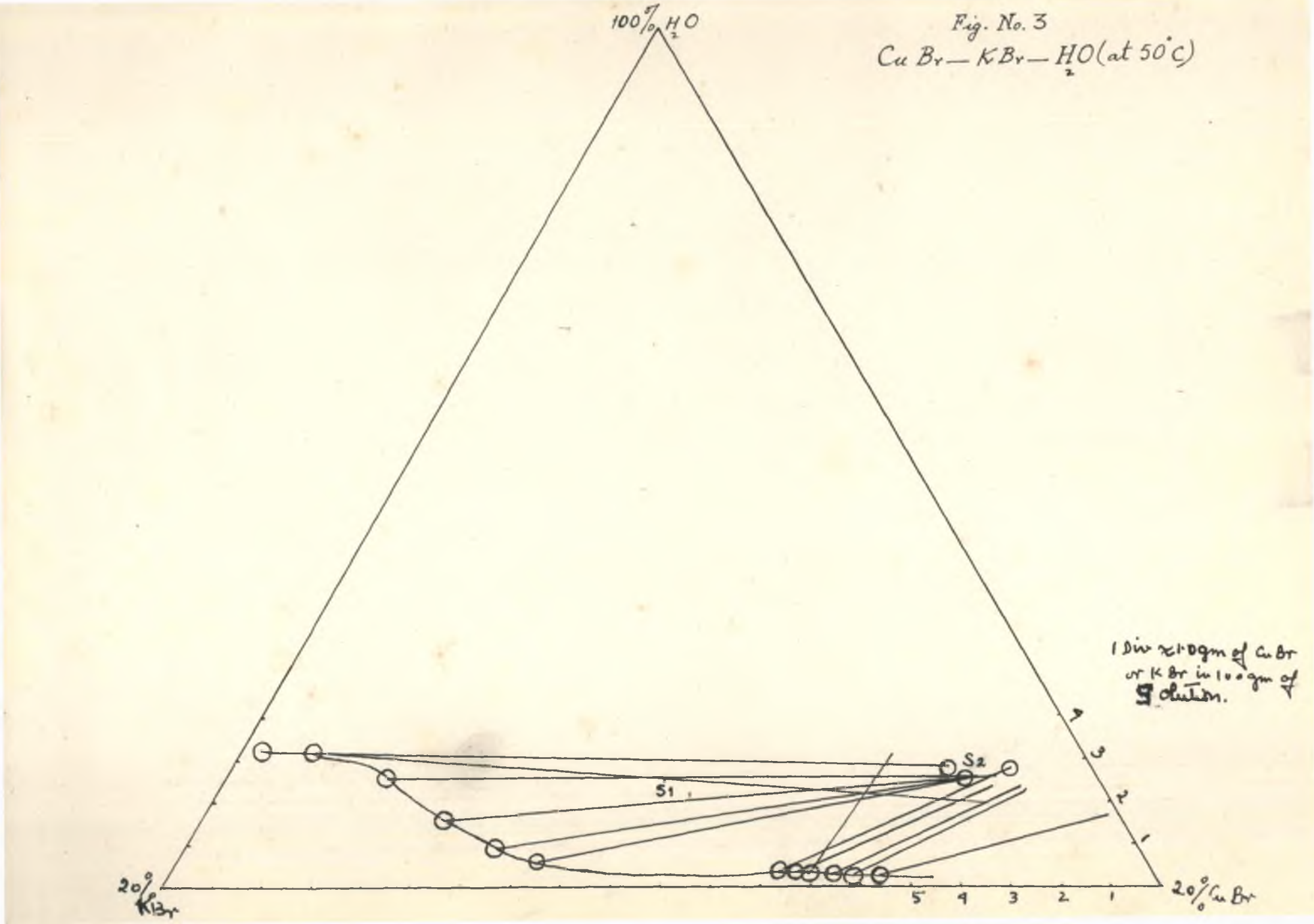

100% H_2O
Fig. No. 3
Cu Br — K Br — H_2O (at 50°C)
1 Div = 1·0 gm of Cu Br or K Br in 100 gm of Solution.
S1
S2
20% K Br
20% Cu Br
5 4 3 2 1
4 3 2 1

Table 1.

System CuBr - KBr - H_2O (at 20°C).

B.T. No.	SOLUTION CuBr %	KBr %	H_2O %	ORIGINAL CONCENTRATION CuBr%	KBr%	H_2O %	WET RESIDUE CuBr %	KBr %	H_2O %
1.	5.37	24.82	69.81	5.37	24.82	69.88	-	-	-
2.	4.57	21.19	74.24	4.83	22.83	72.34	0.26	1.14	98.60
3.	3.83	17.77	78.40	4.29	19.85	75.86	0.46*	2.03*	97.51*
4.	2.98	15.67	81.35	3.75	17.37	78.88	0.77*	1.70*	97.46*
5.	1.90	13.92	84.18	3.22	14.89	81.89	1.22	0.97	97.81
6.	1.65	11.62	86.73	2.68	12.41	84.81	1.03	0.79	98.18
7.	1.20	9.22	89.58	2.23	9.92	87.85	1.03	0.70	98.27
8.	0.93	6.46	93.64	1.61	7.44	90.95	0.68	0.98	98.34
9.	0.57	4.59	94.84	1.07	4.96	93.97	0.43	0.37	99.20
10.	0.20	2.06	97.74	0.53	2.48	96.99	0.33	0.42	99.25

Fig. 1.

Table 2.

CuBr - KBr - H_2O (at 50°C)

B.T. No.	SOLUTION CuBr gm/lit	KBr gm/lit	ORIGINAL CONCENTRATION CuBr gm/lit	KBr gm/lit	WET RESIDUE CuBr gm/lit	KBr gm/lit
1.	75.2	223.6	75.2	223.6	-	-
2.	65.4	185.39	71.4	212.41	6.0*	27.02*
3.	58.2	170.31	67.6	201.22	19.4*	30.01*
4.	41.5	164.3	63.9	190.06	20.4*	25.7 *
5.	33.3	152.6	60.2	178.8	26.9*	26.2 *
6.	31.6	140.9	56.3	167.7	24.7	26.8
7.	26.4	134.6	52.6	156.5	26.2	21.9
8.	20.3	128.9	48.8	145.3	28.5	16.4
9.	15.87	120.3	45.1	131.3	29.3*	10.8 *
10.	8.71	73.03	41.03	122.98	22.6*	49.9 *
11.	6.88	70.98	37.5	111.6	30.6	40.7
12.	4.9	69.1	33.8	100.6	28.9	30.5
13.	3.9	63.4	30.72	88.4	26.8	25.0
14.	3.6	62.6	26.3	78.2	22.7	15.6
15.	3.2	61.2	21.5	67.08	18.3	5.8
16.	2.8	54.8	19.68	55.91	16.8	1.1

Fig. 2.

Table 3.

$CuBr - KBr - H_2O$ (at $50^{\circ}C$)

B.T. No.	SOLUTION CuBr%	KBr%	H_2O %	ORIGINAL CONCENTRATION CuBr %	KBr %	H_2O %	WET RESIDUE CuBr %	KBr %	H_2O %
1.	7.52	22.36	70.12	7.52	22.36	70.12	-	-	-
2.	5.82	18.53	75.64	7.14	21.24	71.62	0.60	2.7	96.2
3.	4.15	17.03	78.82	6.76	20.12	73.12	1.94	3.0	95.06
4.	3.33	16.43	80.24	6.39	19.00	74.61	2.04	2.57	95.39
5.	3.16	15.26	71.58	6.02	17.88	76.10	2.69	2.62	94.69
6.	2.64	14.09	83.27	5.63	16.77	77;6	2.47	2.68	94.85
7.	1.58	13.46	84.96	5.26	15.65	79.19	2.62	2.19	94.19
8.	0.871	12.89	86.29	4.88	14.53	80.59	2.85	1.64	95.51
9.	0.688	12.03	87.28	4.51	13.11	82.38	2.93	1.08	95.91
10.	0.49	13.03	92.21	4.13	12.29	82.58	2.26	4.99	92.75
11.	0.39	7.098	92.51	3.75	11.16	85.09	3.06	4.07	92.87
12.	0.36	6.91	92.73	3.38	10.06	86.56	0.089	3.05	94.06
13.	0.39	6.34	93.27	3.07	8.84	87.09	2.68	2.50	94.82
14.	0.36	6.26	93.38	2.63	7.82	89.55	2.27	1.56	96.17
15.	0.32	6.12	93.56	2.15	6.708	91.15	1.83	0.58	96.59
16.	0.28	5.48	94.24	1.968	5.59	92.44	1.68	0.11	98.21

Fig. 3.

Conductometric And Potentiometric Studies

The conductometric and potentiometric studies were done using the same stock solution (as was taken during analytical studies) and all the observations were made with mixtures kept immersed in the thermostatic bath at $50 \pm 0.1^{\circ}C$. The cuprous bromide and water were mixed in the same order as for the analytical studies.

The conductometric studies were carried out with a

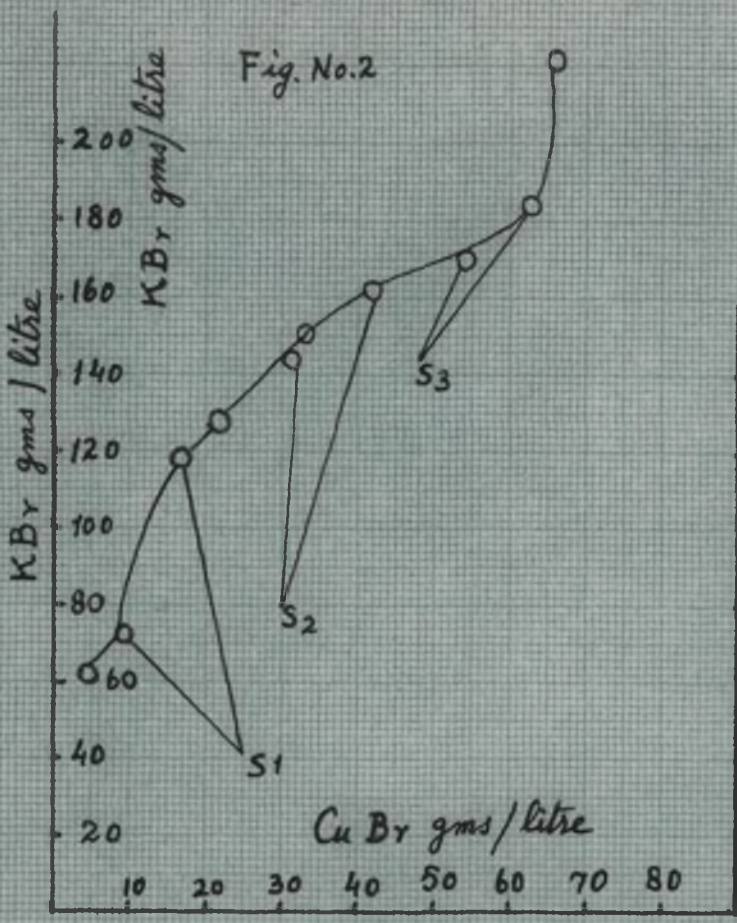


Fig. No.2

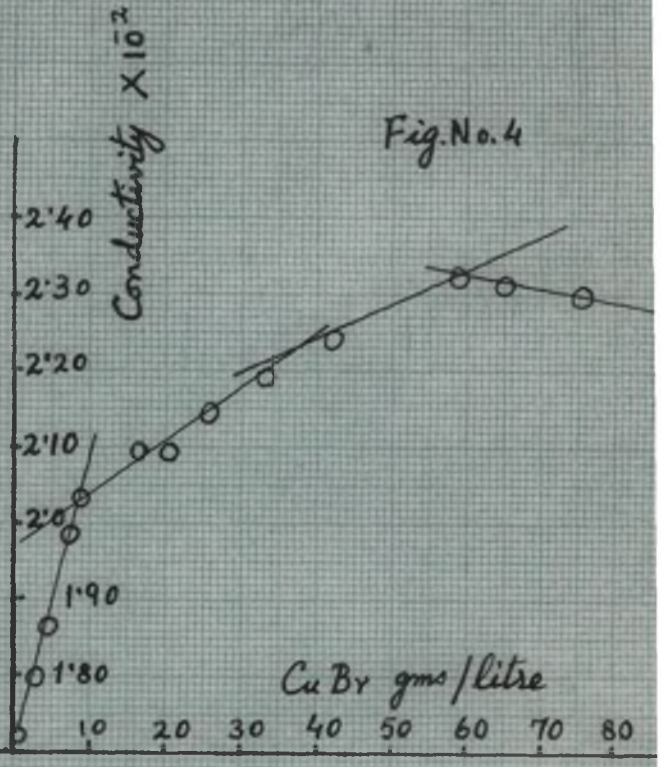


Fig. No.4

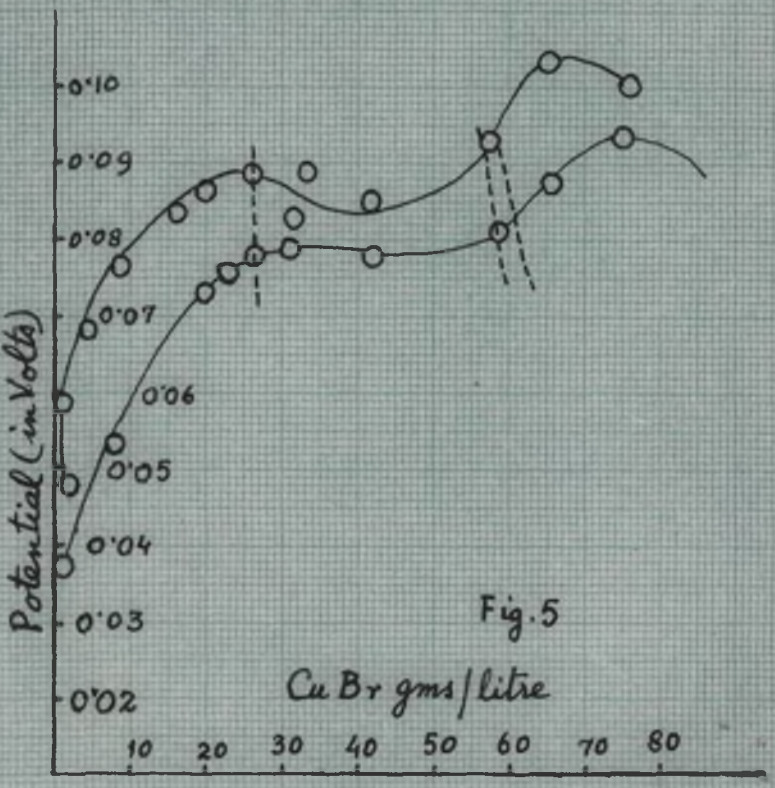


Fig. 5

W.TW conductivity bridge and dip type conductivity cell, for measuring solutions of high conductance a wheat stone bri system with a spread of 500 cm. in conjunction with W.C.Pye resistance box and oscillator and head phone were used.

The e.m. F measurements were made with the help of a clean platinum wire indicator electrode dipped in cuprous solution thus forming $Cu^{+} \rightleftharpoons Cu^{++} + e$ using the standard calomel electrode couple as the reference. A Tinsely Vernier potentiometer with a lamp scale arrangement was used for determining the potential. In order to check the reversibili of measurements a number of readings were taken for the same sample.

The results of potentiometric and conductometric studie are summerised in the following table.

Table .

CuBr gms/lit	KBr gms/lit	Conductance $x10^{-2}$	Potential (in volts)	Potential (in volts)
75.2	223.6	2.30	0.102	0.092
65.4	185.39	2.31	0.105	0.087
58.2	170.31	2.33	0.091	0.079
41.5	164.3	2.25	0.083	0.078
33.3	152.6	2.21	0.082	0.076
31.6	140.9	-	-	-
26.4	134.6	2.16	0.088	0.078
20.3	128.9	2.09	0.085	0.075
15.87	120.3	2.10	0.082	0.071
8.71	73.03	2.04	0.078	0.052
6.88	70.98	1.99	-	-
4.90	69.1	-	-	-
3.90	63.4	1.87	0.058	-
3.60	62.6	-	0.053	-
3.20	61.2	-	0.048	-
2 .80	54.8	1.80	0.038	0.038
		Fig. 4.	Fig. 5.	

Fig. No. 6

System Cu Br — HBr — H_2O (at 50°C)

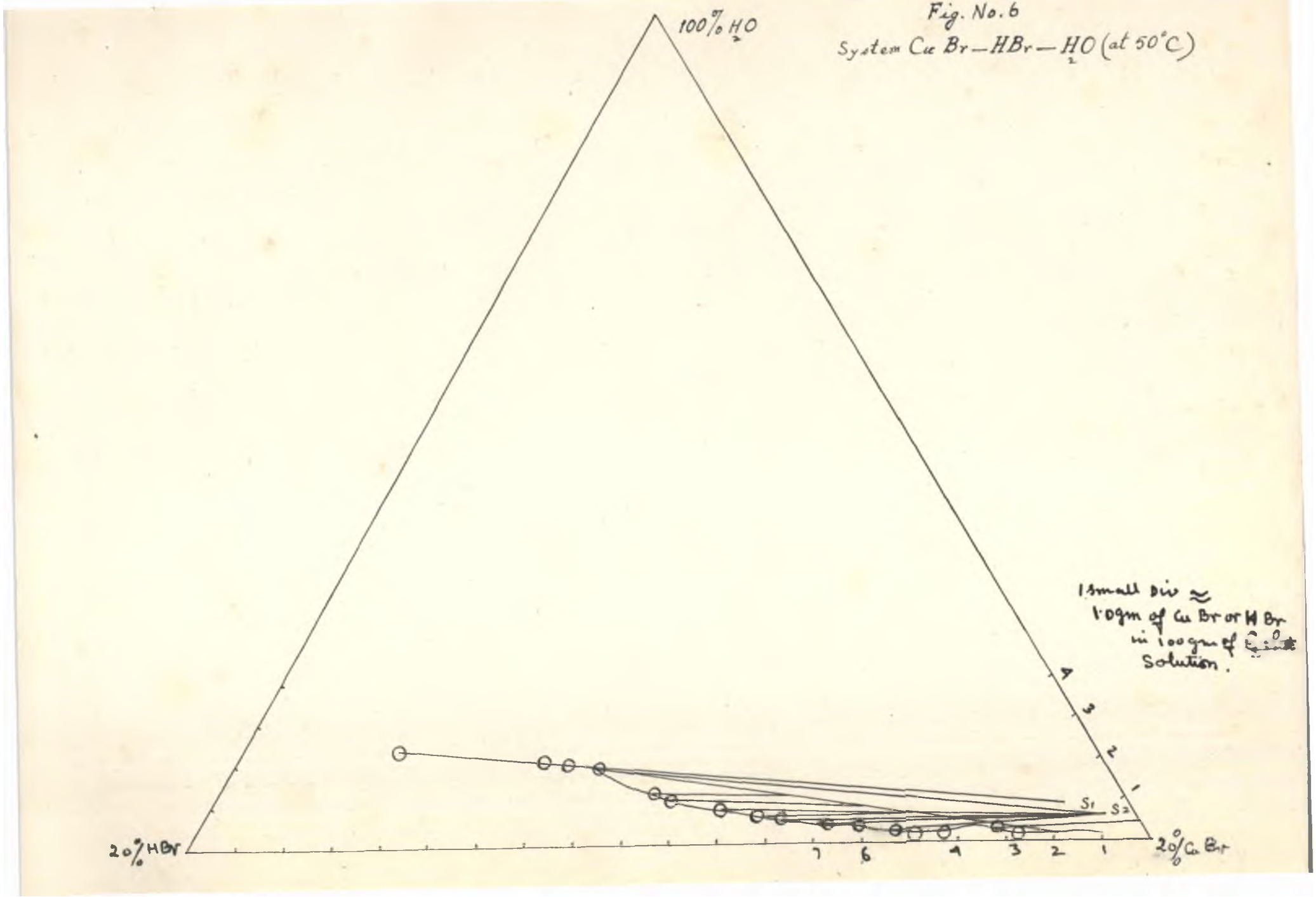


Table 5.

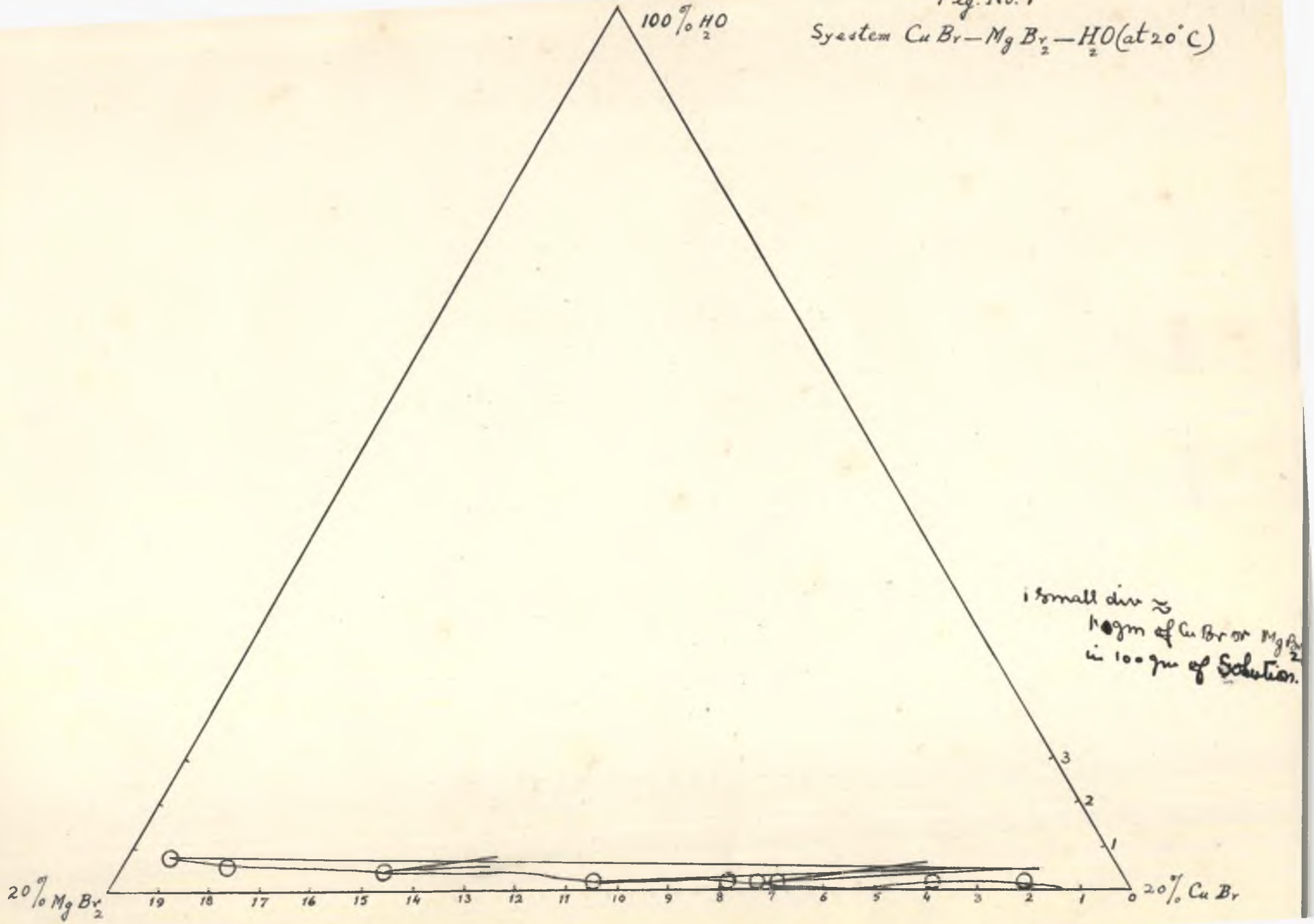
CuBr - HBr - H_2O (at 50°C)

B.T. No.	SOLUTION CuBr%	HBr%	H_2O %	ORIGINAL CONCENTRATION CuBr %	HBr %	H_2O %	WET RESIDUE CuBr %	HBr %	H_2O %
1.	2.39	14.13	83.48	2.39	14.13	83.48	-	-	-
2.	2.20	11.52	86.28	2.27	13.43	84.30	0.07	0.90	99.03
3.	2.06	11.65	86.29	2.15	12.73	85.12	0.09	1.078	98.83
4.	1.85	11.07	87.08	2.02	12.04	85.94	0.168	0.97	98.86
5.	1.57	10.48	87.95	1.90	11.31	86.69	0.33	0.823	98.85
6.	1.29	9.61	89.10	1.78	10.63	87.59	0.49	0.91	98.60
7.	1.06	9.46	89.48	1.66	9.89	88.45	0.60	0.33	99.07
8.	0.96	8.59	91.45	1.54	9.19	89.27	0.58	0.59	98.83
9.	0.70	7.85	91.45	1.42	8.48	90.10	0.72	0.51	98.77
10.	0.61	7.42	91.97	1.30	7.79	91.01	0.69	0.36	98.95
11.	0.43	6.55	93.02	1.18	7.06	91.76	0.75	0.40	98.85
12.	0.48	5.82	93.70	1.07	6.36	92.57	0.58	0.43	98.99
13.	0.35	5.24	94.41	0.94	5.65	93.41	0.60	0.30	99.10
14.	0.30	4.80	94.90	0.81	4.95	94.24	0.51	0.13	99.46
15.	0.28	4.11	95.61	0.71	4.25	95.04	0.43	0.14	99.43
16.	0.18	3.44	96.38	0.59	3.53	95.88	0.41	0.08	99.51
17.	0.23	2.75	97.02	0.47	2.82	96.71	0.14	0.069	99.81
18.	0.15	2.06	97.79	0.35	2.12	97.53	0.072	0.058	99.87
19.	0.0741	1.37	98.56	0.20	1.41	98.39	0.14	0.031	99.83
20.	0.037	0.69	99.17	0.12	0.707	99.18	0.081	0.016	99.9

Fig. 6.

Fig. No. 7

System $CuBr - MgBr_2 - H_2O$ (at 20° C)



1 small div ≈
1 gm of $CuBr$ or $MgBr_2$
in 100 gm of Solution.

Table 6.

CuBr - MgBr - H_2O (at 20°C)

B.T. No.	SOLUTION CuBr %	$MgBr_2$ %	H_2O %	ORIGINAL CONCENTRATION CuBr %	$MgBr_2$ %	H_2O %	WET RESIDUE CuBr %	$MgBr_2$ %	H_2O %
1.	1.46	23.43	75.11	1.46	23.43	75.11	-	-	-
2.	0.94	18.42	80.64	1.31	21.08	79.61	0.37	2.66	96.97
3.	0.75	17.30	81.95	1.17	17.94	80.89	0.42	0.64	98.94
4.	0.55	14.25	85.20	1.02	16.40	82.58	0.47	2.15	97.48
5.	0.32	10.32	89.36	0.87	14.05	85.08	0.52*	3.73*	95.75*
6.	0.24	7.60	92.16	0.73	11.71	87.56	0.49*	3.81*	95.70*
7.	0.23	7.26	92.51	0.58	9.37	90.05	0.35	2.11	97.54
8.	0.21	6.95	92.84	0.43	7.02	92.55	0.22	0.07	99.71
9.	0.15	3.78	96.07	0.29	4.68	95.03	0.14	0.90	99.06
10.	0.13	2.13	97.74	0.14	2.34	97.52	0.01	0.21	99.7

Fig. 7.

D I S C U S S I O N

The results on chemical analysis (represented in the form of triangular phase rule curves Fig. 1 and 3 and rectangular phase diagram Fig. 2) have been able to give precise information regarding the complexes formed in the solid as well as liquid phase for the system CuBr - KBr - H_2O at 20^o and 50^oC respectively. The results are summarised in the following table.

Table 7.

Fig.No.	Triangular curve No.	% of CuBr and KBr in solid phase calculated from the tie point.	Molar ratio in the solid phase	Complexes fromed	Molar ratio in the liquid phase	Complexes formed.
		CuBr-KBr-H_2O at 50°C				
Fig.3	1.	8.6 KBr, 2.6 CuBr S_1	1:4	K_4CuBr_5	1:5	CuBr.5KBr
		2.6 KBr, 2.6 CuBr S_2	1:1.3	$KCuBr_2$	1:10	CuBr.10KBr
		CuBr-KBr-H_2O at 20°C				
Fig.1.	1.	0.80 KBr, 1.0 CuBr S_1	1:1	$KCuBr_2$	1:6	CuBr.6KBr
	rectangular curve No.	CuBr-KBr-H_2O at 50°C				
Fig.2.	1.	40.0 KBr, 25.0 CuBr S_1	1:1.8	K_2CuBr_3	1:2.8	K_3CuBr_4
		77.0 KBr, 33.0 CuBr S_2	1:2.8	K_3CuBr_4	1:50	CuBr.5KBr
		146.0 KBr, 48.0 CuBr S_3	1:3.6	K_4CuBr_5	1:10	CuBr.10KBr

The results of chemical analysis were further confirmed by electrometric methods. The conductometric measurements indicate the formation of complex K_3CuBr_4 and addition compounds CuBr.5KBr and CuBr.10KBr in the aqueous phase, potentiometric measurements also provide the same information regarding the composition of the complexes in aqueous phase. The results are tabulated below.

Table 8.

$CuBr-KBr-H_2O$ at 50°

Fig. No.	Conc. of KBr and CuBr gms/ lit at the point of intersection	Molar ratio	Complexes formed	Fig. No.	Conc. of KBr and CuBr gms/lit	Molar ratio	Complexes formed
4.	73.03 KBr 8.71 CuBr S_3	1:10	CuBr.10KBr	5.	58.2 CuBr 170.31 KBr S_1	1:28	K_3CuBr_4
	152.15 KBr 33.3 CuBr S_2	1:5.4	CuBr.5KBr		33.3 CuBr 152.6 KBr S_2	1:54	CuBr.5KBr
	170.31 KBr 58.2 CuBr S_3	1:2.8	K_3CuBr_4		58.2 CuBr 170.31 KBr S_1	1:28	K_3CuBr_4
					41.5 CuBr 164.3 KBr S_2	*:4.8	CuBr.5KBr

From the results obtained by the chemical analysis of aqueous phase, it may be concluded that at relatively high temprature there is higher solubility of cuprous bromide in potassium bromide and with increasing concentration of KBr the complexes ranging from K_4CuBr_5 to $KCuBr_2$ are formed; however in solutions there is little tendency of complex ion formation and there was no complex formation at 20°C, only the complex K_3CuBr_4 at 50°C can be said to exist. The other compounds like CuBr.5KBr, CuBr.10KBr etc. are probably addition compounds or may indicate the solubility of cuprous bromide in potassium bromide. The electrometric studies also confirm the results of chemical analysis.

The systems CuBr - HBr - H_2O (at 50°C) and CuBr - $MgBr_2$ - H_2O (at 20°C) were also studied analytically There was no indication of complex formation in the aqueous phase, only, the complexes CuBr.3HBr and CuBr.3$MgBr_2$ formed in the solid phase. The results are summarised in the following table.

Table 9.

Fig. No.	Triangular curve No.	% of CuBr and XBr in solid phase calculated from the point.	Molar ratio	Complexes formed	Molar ratio in the aqueous phase	Complexes formed
6.	1.	0.60 CuBr, 1.10 HBr — S_1	1:3	H_3CuBr_4	1:25	CuBr.25 HBr
7.	1.	0.55 CuBr, 2.50 $MgBr_2$ — S_1	1:3	Mg_3CuBr_7	1:25	CuBr.25 $MgBr_2$

Indirect evidence of the form in which cuprous bromide exist in the solution is also forthcoming on the basis of these studies and the possibility of the existence of addition products like CuBr.25 HBr and CuBr.25 $MgBr_2$ can not be wholly ruled out. That such addition products with practically indefinite molecules of XBr (X= H, K and Mg) associated with them is quite possible in view of the low solubility of CuBr in aqueous bromide solutions at the ordinary temprature.

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A P P E N D I X

A P P E N D I X

CHEMICAL ANALYSIS AND MAGNETIC MEASUREMENTS OF SOME COMPLEXES OF CHROMOTROPIC ACID, CHROMOTROPE 2B, ETHANOLAMINE AND HYDRAZIN

The results on the composition of Cu (i), Cu (ii) and V (iv) complexes of chromotropic acid and Cu (ii) complex of chromotrope 2B employing physical methods have already been discussed earlier (Chapters I and II). In order to get more conclusive information regarding their composition, it was thought worthwhile to study them by methods of chemical analysis and magnetic susceptibility. A brief account of the results chemical analysis and magnetic measurements is given below.

1. Results of Chemical Analysis:

(a) Cu (i), Cu (ii) and V (iv) complexes of chromotropic acid and Cu (ii) complex of chromotrope 2B.

The complexes were isolated by extracting them with organic solvents. The conditions of isolation are depicted in the following table.

Table 1.

Complex	Ratios of the reactants	Reagent used
Cu (i) - D.N.S.	2:1	Acetone
Cu (ii)- D.N.S.	1:1	Mixture of Acetone and Ethyl acetate (1:2)
V (iv)- D.N.S.	1:1	Mixture of Acetone and Ethyl acetate (1:2)
Cu (ii)- Chromotrope 2B	1:1	Mixture of Acetone and Ethyl acetate (1:3)

The products thus obtained were dried over CuO for more than 24 hours. The following are some of the physical properties of the substances:

Table 2.

Complex	Solubility	Colour of the dry product	Colour of the solution	Density
Cu (i) - D.N.S.	slightly soluble	brown	pink	1.24
Cu (ii)- D.N.S.	soluble	reddish brown	red	1.09
V (iv)- D.N.S.	soluble	black	reddish brown	1.24
Cu (ii)- Chromo-trope 2B	very soluble	brownish black	violet	1.20

Analysis of the complexes:

The amount of copper present in the complexes was estimated as follows:

A known weight (about 0.5g) of the dried sample was fused with oxidising fusion mixture (mixture of sodium and potassium carbonate and potassium nitrate). After completion of the fusion, the fused product was dissolved in hot water, when copper separated as copper oxide and the whole mass was filtered (the filterate was kept for sulphur estimation), CuO being insoluble remained on the filter paper and washed with hot water number of times and dissolved in pure dil HCl. To the acidic solution thus obtained a few drops of phenolphth-alein was added and was treated with potassium hydroxide (A.R.) until copper was precipitated as copper hydroxide (excess of alkali was indicated by the development of pink colour). The precipitate of copper hydroxide was washed with hot water several times and finally dissolved in dil H_2SO_4 (A.R.). The copper sulphate solution thus obtained was estimated iodometrically and the amount of copper present in the substance was determined.

The sulphur present in the complex was estimated as $BaSo_4$. The filterate obtained after fusion of the complex, was acidified with HCl and warmed, to the warmed solution $BaCl_2$ solution was added, when the latter was precipitated as

$BaSO_4$. It was weighed as $BaSO_4$ and the amount of sulphur was estimated.

The amount of vanadium in the sample was estimated, by dissolving the complex in dil H_2SO_4 and reducing the resulting acidic solutions on Jone's reductor and titrating it against standard $KMnO_4$ (details given in Chapter I, page 24).

The following are the results of the analysis of the complexes.

Complex	Calculated	found	composition
Cu(i) - D.N.S.	Cu 20.3% S-10.2%	Cu-18.6%-S-9.4%	Cu_2(D.N.S.
Cu(ii)- D.N.S.	Cu 14.92% S-14.54%	Cu-15.9%;S-10.92%	Cu (D.N.S.
V (iv)- D.N.S.	V-11.88%;C-27.97%	V-12.2%;C-20.83%	VO(D.N.S.
	H-0.93%;S-14.09%	H-2.47%;S-13.19%	
	O-45.13% (by difference)	O-52.4% (by difference)	
Cu(ii)-Chromotrope 2B	Cu-11.02%; S-11.0%	Cu-10.2% ;S-10.5%	

b) <u>Cr (ii), Cr (iii) hydrazine complex:</u> The amount of chromium in the dried samples was estimated gravimetrically by weighing it as Cr_2O_3:

A known quantity (about 0.5g) of the dried sample was dissolved in dil HNO_3 to the acidic solution thus obtained ammonia was added in excess when chromium was precipitated as chromium hydroxide, the solution was boiled and fittered on a (fitterate was kept for chloride estimation) gravimetric fitter paper. Chromium hydroxide was washed with hot water several times and then dried ignited and weighed as Cr_2O_3.

To the boiled filterate (containing little amount of nitric acid). $AgNO_3$ was added when chloride was precipitated as AgCl, it was fittered over sintered crucible, washed with dil HNO_3 and hot water several times and weighed as AgCl.

The amount of hydrazine in the sample was determined by the indirect iodate method.

A weighed amount of the substance (about 0.5g) was dissolved in dil HCl, to the acidic solution thus obtained a known quantity of KIO_3 solution was added when KIO_3 reduces to iodine, the iodine thus liberated was estimated by titrating the solution against sodium thio sulphate.

The results of analysis are as follows:

Complex	Perdentage of elements estimated	emperical formula of the complex
Cr (ii)-hydrazine	Cr-19.5%; Cl-23.1%; N_2H_4-34% H_2O 22.8%	$CrCl_2.3N_2H_4.3H_2O$
Cr(iii)-hydrazine	Cr-34.2%; N_2H_4- 5.7% Cl-60.1% (by difference)	$CrCl_3.3N_2H_4$

c) Vanadyl-Ethanolamine complexes:

The complexes of ethanolamines were isolated by treating the concentrated solution complex ($2x10^{-2}$M) with acetone, and drying the extracted product in vacuum desiccator over CaO for over 48 hours. The products were highly hygroscopic but quite stable in air.

The results of the analysis of the complex are summarised in the following table.

Complex	Calculated	found	Composition
V(iv)- Monoethanol amine	V-20.5%; H-3.7% C-12.06%; N-7.03% Cl-35.6% O(by difference)- 21.11%	V-19.5%; H-3.96% N-5.15% C-12.34% Cl-34.5% O(by difference)- 24.55%	VO^{++} (M.E.) Cl_2
V(iv)-Diethanol-amine	V-14.36%	V-15.6%	$VO(D.E.)_2$ Cl_2
V(iv)-Triethanol-amine	V-13.80%	V-15.02%	$VO(T.E)_2$ Cl_2

Note: C, H and N estimations were carried out by the courtsey of Micro analytical department (organic section) (University of Melbourne, Australia).

2. Magnetic Susceptibility measurements:

The magnetic measurements were carried out with the help of Gouy's magnetic balance having temperature control arrangement in the Chemistry department, M.S. University of Baroda (Courtesy Dr. J.S. Dave).

Following are the results of magnetic susceptibile by data of the complexes.

Complex	Mass susceptibility $\chi \times 10^{-6}$	Tamprature °C	Remarks
Cu (i) - D.N.S.	- 1.237	31.5°C	diamagnetic
Cu (ii) -chromotrope 2B	17.63	32.5°C	paramagnetic
V (iv) -monoethanol-amine	- 0.3645	30°C	diamagnetic
Cr (ii)-hydrazine	2.29	32.8°C	paramagnetic
Cr (iii)-hydrazine	36.496	32°C	paramagnetic

The values of Molar susceptibility χ_M and effective magnetic moment Ueff calculated (from the above data are as follows:

Complex	χ_M	Ueff= 2.83 $\sqrt{\chi_M T}$	No. of unpaired electron	Expected number of unpaired electron
Cu (i) - D.N.S.	6.05×10^{-4}	-	-	-
Cu (ii)-Chromotrope 2B	1.01×10^{-2}	5.08	4	1
V (iv)-monoethanol-amine	2.23×10^{-5}	-	-	-
Cr (ii)-hydrazine	5.10×10^{-2}	3.4	2	2
Cr(iii)-hydrazine	1.85×10^{-2}	-	-	-

D I S C U S S I O N

The results on the chemical analysis of Cu (i), Cu (ii) and V (iv) complexes of chromotropic acid (sodium salt) point towards the formation of 2:1 (Cu^{+} and D.N.S.), 1:1 (Cu^{++} and D.N.S.) and 1:1 (VO^{++} D.N.S.) complex. Although the percentage values estimated were found to differ from the theoretical values (and differ widely in certain cases), Nevertheless, the estimated values give composition approaching to those found by spectrophotometric and other physical methods.

The analysis of Cu (ii) - chromotrope 2B complex also confirms the results obtained by the spectrophotometric methods regarding the composition of 1:1 product.

The composition of chromous hydrazine complex investigated by physical methods (Chapter V) gave the information for 1:3 $CrCl_2$ and hydrazine complex. The results on chemical analysis also gave the same information together with 3 moles of H_2O. The formula of the complex thus may be written as $CrCl_2.3N_2H_4.3H_2O$.

The analysis of the Cr (iii)-hydrazine complex gave the information for 3:1 chromic to hydrazine complex. The estimated values of Cr and N_2H_4 were nearly the same as that of theoretica values but surprisingly enough the percentage of Cl came out to be 13.3% far too low from the calculated value. The percentag

of Cl, therefore, determined by difference .

The results obtained by the chemical analysis of vanadyl-ethanolamine complexes showed the formation of 1:1, 1:2 and 1:2 vanadyl-monoethanolamine-diethanolamine and- triethanolamine complexes respectively.

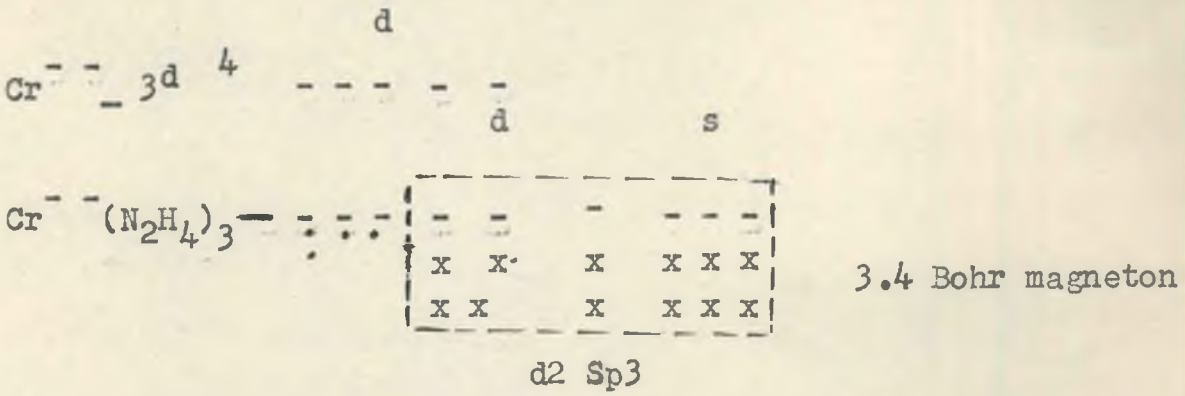
The composition of 1:1 VO^{++} to monoethanolamine complex is established (physical methods gave the information of 1:2 and 2:3 vanadyl- monoethanolamine complex), the validity of information for 1:2, 1:2 vanadyl-eiethanolamine and vanadyl-triethanolamine complex is doubted as only the estimated metal percentage approaches to the calculated values, otherwise the C, H, N estimated values differ widely from the theoretical values.

The magnetic susceptibility measurements of some of the complexes of chromotropic acid, chromotrope 2B and hydrazine gave intresting information regarding the structure and bonding in the complex.

The Cu (i)- D.N.S. complex is diamagnetic as it should not have any unpaired electron, on the other hand Cu (ii)-chromotropic complex is paramagnetic as expected generally from the Cu (ii) complexes. However the value of effective Bohr magneton (5.08) point towards the existence of 4 unpaired electrons instead of one. Such a discrepancy is however, not striking since cases are met with where the observed number of

unpaired electrons differ widely from those theoretically predicted (Selwood, 'Magneto Chemistry' Inter Science Publishers (New York (1943).). It is quite likely that orbital magnetism is contributing factors in these instances.

The Cr (ii)-hydrazine complex gave a value of magnetic moment as 3.4 Bohr magneton which indicates the presence of two unpaired electrons and thus confirming the results arrived at by the physico-chemical methods.



The formula of the complex thus written as (Cr $(N_2H_4)_3$) $Cl_2.3H_2O$. The Cr (iii)-hydrazine complex is paramagnetic and has a large Bohr magneton value of 6.7, which may again due to the presence of orbital magnetism in the complex.

R E S U M E

R E S U M E

Coordination through nitrogen or the hydroxyl group of the complexing agent is not something unusual in the field of inorganic chemistry. Examples where chelation would take place with both nitrogen and hydroxyl group as electron donor species are also not very uncommon. Inspite of this, the fact remains that more and more useful information about such compounds is being made available every year and many unexplored waters have yet to be navigated. Problems connected with the use of new complexing agent; study of some less familiar complex ion forming reactions combined with their possible applicability in analytical chemistry; stabilisation of unstable ions through complex ion formation and aspects relating to their structure and characterisation are as important today as they were some fifty years back. The work, embodied in this thesis, is an attempt in this direction and deals with the study of some of the aspects enumerated above.

Chromotropic acid 1:8 dihydroxy naphthalene 3,6 disulphonic acid and its substituted derivative p nitro benzene azo chromotropic acid is said to undergo chelation with a number of heavy metal ions. However, relatively small amount of work has been done with transitional elements copper, manganse and vanadium. This is particularly true for these

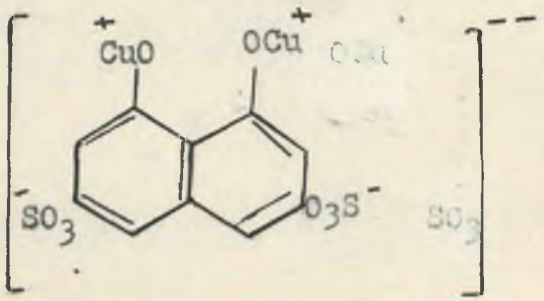
ions in their unstable valence state, viz., Cu (i), V (iv) and Mn (iii). Of the other less known complexing agents, investigations on the complexes with 8 hydroxy quinoline 7 iodo 5 sulphuric acid and Ethanolamines are worth undertaking. Another less familiar reaction is the interaction of Cr (ii) and Cr (iii) with hydrazine. The reaction, although well known, remain almost uninvestigated and deserves a more systematic approach. The concluding pages of the work describe studies on an aspect, though not directly connected with the type of coordination under discussion, is interesting enough and deals with the studies on bromo complexes of Cu (i) with alkali and alkaline earth bromide, employing phase rule and electrometric methods.

Interaction of Cu (i and ii), Mn(iii) and V(iv) with chromotropic acid (D.N.S.).

(a) Conductometric and spectrophotometric methods were employed to study the interaction between cuprous chloride and chromotropic acid (sodium salt) and takes 6 to 12 hours for completion depending upon the concentration of the reactant used (Conc. 2.5×10^{-3} to 1×10^{-3}M six to twelve hours; Conc. 1×10^{-2} to 2.5×10^{-3}M upper limit six hours). Moreover, the reaction was specific for a narrow pH range (5.0 to 7.0) and no indication for complex ion could be realised in either of the extreme pH range (Table.6., Fig. 5., Chapter I p.p.40).

Vosburgh and Cooper's method gave the existence of one complex at 430 mu (p 31). The Job's method of continuous variation gave the ratio 2:1 (Cu : D.N.S.) and so also the slope ratio method (pp 33-35).

The composition of the complex was also confirmed by the modified slope ratio method. The absorbances of the solutions were plotted against the concentration of the variable components from each end of the X-axis. The point of intersection of the two curves corresponded to the composition of the complex, on the assumption that only one complex was formed. It was found that the composition of the complex again corresponded to Cu : D.N.S. as 2:1 (page 36). The complex can be formulated as Cu_2 (D.N.S.) the structure as



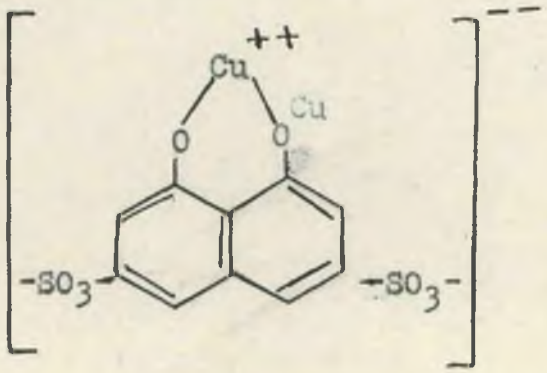
with value of K as $2.1 \times 10^{+4}$ and ΔF^{o} as -2.58 KCals at 30°C (pp 39 and 77).

Conductometric measurements were also made with mixtures prepared according to Job's method of continuous variation. The differences in specific conductivity were plotted against the composition of the mixture (pp 65, 66 and 67). From the curves

the combining ratio was found to be 2:1 (Fig. 18, curve (1) and (2), p. 77).

(b) Cupric chloride and the sodium salt of chromotropic acid interact to give a soluble complex, red in colour. The reaction was quite slow and took two to three hours for completion in the concentration range 2.5×10^{-3}M to 5×10^{-4}M. With more dilute solutions the time for completion increased considerbly and sometimes it took twelve hours for the red colour to develop.

The complex was studied spectrophotometrically and by polarography. On applying Voshburgh and Cooper's method (p 42) it was found that only one absorption maxima at 525 mu is formed. Job's method of continuous variation (pp 43-44) as well as the slope ratio method (pp 45-46) gave the combining ratio as 1:1 and hence the existence of the following chelate:



The formation constant and free energy of complex in solution was also calculated and found to be $2.28 \times 10^{+5}$ and - 3.767 KCals at 30°C (pages 49, 80) respectively. The influence

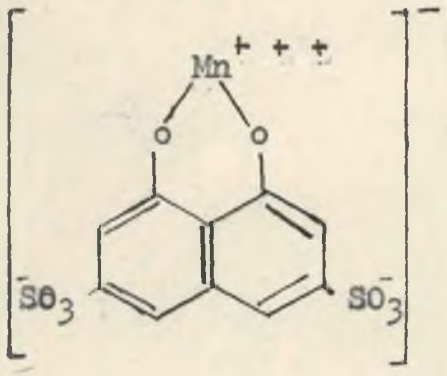
of pH on the reaction was also studied spectrophotometrically and it was found that the reaction could be carried out in the pH range (6.0 to 11.0). No evidence for complex ion formation was available below pH= 6.0 (pp 47-48,80).

Polarograms of the mixtures in different buffers were taken in the pH range 6.0 to 11.0 In all about forty polarogram were taken. From these it was concluded that the complex, Cu^{ii}-D.N.S., is reversibly reduceble at the dropping mercury electrod and reaction took place with one electron transfer (pp. 72, 74, 81). Also on plotting, st. line curves between $E1/_2$ and log Conc the slope of the st. line indicate the formation of 1:1 complex, and furthur the $E1/_2$ versus pH rectilinear curve gave a slope of 0.033 showing thereby that two hydroxyl groups coordinate with one atom of copper (pp. 81-82, 74). The polarographic studies thus confirmed the earlier results arrived at spectrophotometrically.

(c) The interaction between manganic sulphate and chromotropic acid (sodium salt) results in the formation of a yellow coloured complex. The reaction took place in highly acidic medium and has not been studied until now. Spectrophotometric and potentiometric studies were carried out to study the composition of the complex.

Vosburgh Cooper's method indicated the existence of only one complex with λ_{max} at 430 mu (pp. 51,52). Both, the Job's method as well as the slope ratio method gave the combining rati

as 1:1 (pp. 53-56). The complex may be formulated as



The value of K was found to be 1.8×10^{5} and that of ΔF^{o} = - 3.11 KCals at 30°C (page 57, 84).

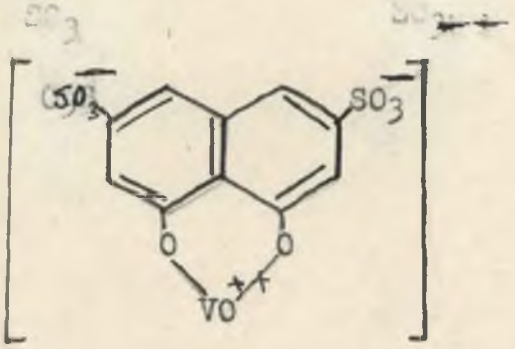
The reaction was found to be interesting from another view point. The formation of a stable complex and the development of the bright yellow colour (acid medium) could be used as a means for the colorimetric estimation of Mn (iii) upto as low a concentration as 10^{-4}M.

Potentiometric titrations carried out between manganic sulphate and the acid (Conc. 1×10^{-2}, 5×10^{-3}, 2.5×10^{-3}; 2×10^{-3}M etc.) also gave results confirming the earlier one S on spectrotrophotometry (pp. 68, 69, 85, 86). The reverse titrations did not, however, prove to be of much use. Here no significant break in the curves could be realised.

(d) Vanadyl sulphate gave a reddish pink compound with chromotropic acid (sodium salt) in the pH range (5.0 to 11.0)

Spectrophotometric method was again employed to determine the nature and composition of the complex.

Absorption studies were carried out in the range 400 to 650 mu. The complex gave a single absorption peak at 525 mu (pp. 58-59). Job's method of continuous variation gave the combining ratio as 1:1 (pp 59-60, 87). The slope ratio also gave the same ratio of 1:1 for VO^{++} to D.N.S. (pp 61-62, 87). The complex may be formulated as .



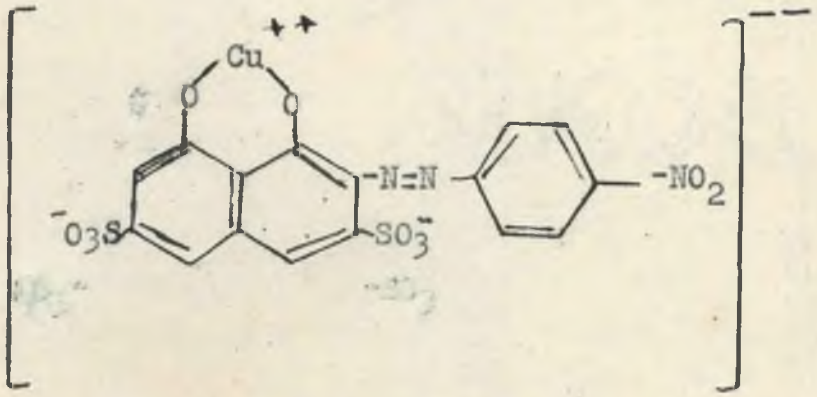
The formation constant and free energy was found to be 3.99×10^3 and - 2.67 KCals respectively at 20°C (p. 64, 88).

Cu (ii)-p-nitro benzene azo chromotropic acid (Chromotrope 2B) reaction:

This reagent forms a violet coloured complex with cupric salts. The compound has an esterfiable phenolic (OH group)

in a coordination position with respect to N atom of the azo group. The chelate binding may be supposed responsible for the colour. The reaction was specific as far as the pH was considered and was stable in the basic range (pH 7 to 11) . (p. 101).

Absorption studies as well as a few polarographic investigations were carried out to understand the nature and the composition of the complex. Vosburgh and Cooper's method showed the existence of one complex with λ_{max} at 550 mu (p. 95, 107). Employing Job's method, it was found that the two reagents combine in the ratio 1:1. The slope ratio gave similar results (pp ,96-100, 107). The complex may be formulated as a chelate with the following structure



with K equal to 5.8×10^{4} and the free energy $-\Delta F^{o} = 2.814$ KCals (p. 102, 108).

Polarographic study of the reaction was also carried out at two different pH's (pH= 7.5 and 11.5) (p.p 104-106 and p.p 108-109). In all about a dozen of polarograms were drawn. The complex was found to be reversibly reducible at the dropping mercury electrode and the reaction was found to take place with one electron transfer ($E\ 3/_4 - E1/_4 = 0.05$). On plotting the $E1/_2$ values against- log Conc. of chromotrope 2B, a st. line was obtained having a slope of 0.05, thus indicating a 1:1 Cu (ii) and chromotrope 2B complex (p. 109).

V (iv)- 8, hydroxy quinoline 7 iodo 5 sulphoric Acid (Ferron).

The reagent is usually employed for the micro determination of iron. The hydroxyl group and the hetro cyclic nitroge of the compound combine with the metal ion to form the chelate ring. Vanadyl sulphate gives a greenish yellow coloured complex with Ferron. The complex was found to be stable in the pH range 2.4 to 9.6 and in this range a single absorption peak at λ_{max} 380 mu was observable (p. 22, 130).

The absorption studies were carried out at 380 mu (Ferron max. 430 mu; vanadyl sulphate 750 mu). Both the Job's method as well as slope ratio method gave the combining ratio as VO^{++} Ferron as 2:3 (p.p 115-121).

The value of formation constant came out to be 2.6×10^4. (p.p 123-124, 129-130).

Furthur confirmation regarding the composition of the vanadyl-Ferron complex was sought for on the basis of conductometry. On plotting differences in specific conductivity (of mixtures prepared according to Job's method) against the composition of the mixtures again a combining ratio of 2:3 (VO^{++}: Ferron) was obtained (pp 125-127, 130).

Although no precise information regarding the structure of the vanadyl Ferron complex could be obtained by either of the two methods employed, the reaction was found quite useful in estimating VO^{++} ion colorimetrically. It was found that Ferron gave quite a sharp colour (greenish yellow) even as low as concentration as 1×10^{-4} M (pp 118-119) in a long pH range of 2.4 to 9.6.

Reaction of vanadyl chloride with Mono-, Di- and Triethanolamines.

(a) Vanadyl chloride forms a soluble complex with mono-ethanolamine. The complex crystallises in fine black crystal and gives a yellowish green colour in aqueous solutions. The nature and composition of the complex was studied by (i) spectrophotometry and (ii) amperometry.

Preliminary experiments revealed the following interesting points regarding the complex.

(i) The reaction was possible only in the concentrated solutions ($2x10^{-2}$M to $5x10^{-3}$M). In relatively higher concentration a turbidity set in.

(ii) The colour of the complex faded on large exposure to air. However on keeping a layer of paraffin on its surface, it was found to be stable for a number of days.

(ii) The greenish yellow colour developed only in the pH range 6.6 to 11.4 and showed the presence of absorption peak at 650 m
(p 139, 143 and 167).

(iii) The black crystals although hygroscopic in nature, were quite stable.

Job's method of continuous variation as well as the slope ratio method (pp 140-142) were employed to know the compositio of the complex (studies carried out at 650 mu). Both the metho gave the combining ratio VO^{++}. monoethanolamine as 2:3.

The complex was found to be non-reducible at dropping mercury electrode. Hence polarographic technique could not be employed. However, amperometry was found to be quite successfu in elucidating the composition of the complex. Amperometric titrations were carried out at -1.0 volt between vanadyl chlori (in the cell) and monoethanolamine as the titrant. Sulphuric

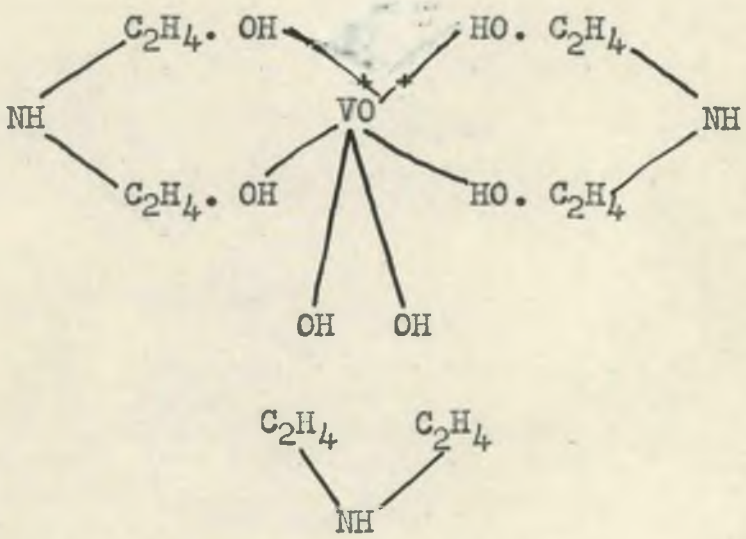
acid was used as acid buffer and supporting electrolyte . The titrations were performed at - 1.0 volt (pp 146-148, 169). Here the results did not coincide with those of spectrophotometr and ratio of 1:2 instead of 2:3 was obtained. The following structure may be given to the complex on the basis of amperometr

$$NH_2 . C_2H_4 . OH- VO^{++} HO . C_2H_4 . NH_2$$

(b) Vanadyl chloride - diethanolamine complex differs only in one respect with its counter part mono ethanol amine, is being quite unstable in air. The complex gives a yellow colour in solution and crystallises in black crystals, which are extremely hygroscopic. Inspite of the fact that it is unstable under ordinary conditions, investigations could be carried out by putting a layer of paraffin on the reaction mixture. The composition was determined by spectrophotometry and amperometry

Application of Vosburgh and Cooper's method indicated the existence of a complex with λ_{max} at 800 mu (p 149, 169). The Job's method and slope ratio method gave the combining ratio of 1:4 and 2:3 respectively (pp 150-153). On plotting the absorption curve at different pH's , the complex was found to give the maximum absorption (λ_{max} = 800 mu) in the pH range 6.6 to 11.4 (p 153, 171).

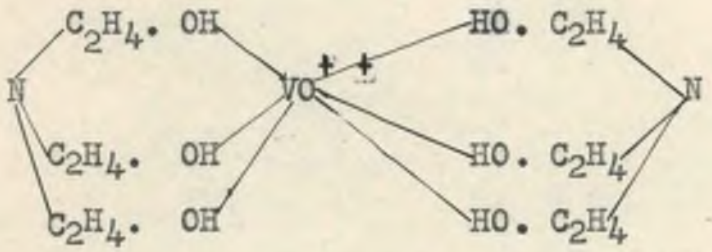
Amperometry of the complex was done under exactly simila conditions as in the case of monoethanolamine complex. Here the ratio was found to be 1:3 (pp 154-155, 171). The following structure may be assigned on the basis of amperometr studies.



(c) Unlike the mono and diethanolamine complexes, the triethanolamine complexe is stabler and gives a greenish yellow coloured complex, crystallising out in well defined black crystals. Its composition was determined spectrophotometrically and by amperometry. The absorption studies, carried out

in the pH range 4 to 11.4 gave a single absorption peak at 850 mu (p 161, 173). Job's method of continuous variation as well as the slope ratio method gave the ratio VO^{++}: Triethanolamine as 2:3 (pp 158-160).

Amperometric titrations carried out between vanadyl ion (in the cell) and triethanol gave typical curves with well defined inflexion points at 1:2 (VO^{++} Triethanolamine). On the basis, the following formula be assigned to the VO^{++} Triethanolamine complex.



The most striking feature of the V (iv)- ethanolamine reaction is, that the spectrophotometric studies do not give reasonably good results leading to precise knowledge about the composition of the complex formed. On the other hand the amperometric titration studies had been able to give the desired information. The discrepancy in the results of the two methods might be attributed to two factors (i) instability

of the complex under ordinary atmospheric condition and (ii) the presence of colloidal precipitates, with these limitation the spectrophotometric method was liable to give less reliabl results. In the amperometric titration, these difficulties could be readily over come, especially the former one, since a measurements were carried out in an atmosphere of nitrogen.

Interaction of Cr (ii and iii) with hydrazine:

A large number of metal hydrazine compounds, including those of transitional metals, have been studied. Very little has, however, been done in respect of chromium compounds. Thi is especially true for the chromous chloride hydrazine reacti

Chromous chloride reacts with hydrazine to give a bluis violet coloured complex, insoluble in water and organic solve The composition of the complex was fully studied in its fresh precipitated state as well as in its dried state by physico-chemical and purely chemical methods.

Amperometric titrations between chromous chloride (in cell) and hydrazine (as the titrant) were carried out at 0-0. volt. The combining ratio $CrCl_2$: N_2H_4 came out to be 1:3 (pp 182-186, 199).

Use was made of the Cr (ii) $\rightleftharpoons$ Cr (iii) +e couple to carry out potentiometric titrations between the two. Sharp

inflexion points could be realised for the various concentra employed and in each case a ratio of 1:3 ($CrCl_2$: N_2H_4) was obtained (pp 186-188, 200).

The complex in its completely washed and dried state wa analysed for chromium, chloride hydrazine and water (see Appendix). The empirical formula came out to be $CrCl_2 . 3N_2H_4 . 3H_2O$ and structure may be written as ($Cr(N_2H_4)_3$) $Cl_2 . H_2O$. The complex was expected to have an octahedral (d^2sp^3) structure with two unpaired electrons. Magnetic susceptibity measurements confirm the above view, as the value of effectiv Bohr magneton came out to be 3.4 which indicates the presence of two unpaired electrons (see appendix).

Chromic chloride gives a bluish green insoluble complex with hydrazine. The composition of the complex could be studied only in the freshly precipitated state. The dried sample could not be fully analysed since the percentage of chloride was always lesser than expected theoretically, an indirect estimation of chloride (after estimating chromium and hydrazin gave fairly satisfactory results.

Amperometric titrations (both direct and reverse) betwee chromic chloride and hydrazine were carried out at -1.2 volt (potential applied, as found out from the pletean of the chromic chloride polarogram) (p 190). The combining ratio was found to be Cr^{+++}: N_2H_4 as 3:1 (pp 190-193, 201-20).

Potentiometric titrations were also carried out. The interesting feature about them was that these experiments could be performed without employing, the Cr(ii)- Cr(iii) couple. Instead, bright platinium dipped in chromic chloride solution worked satisfactorily as an indicator electrode (pp 193-197, 203).

Hydrazine with its strong reducing property is likely to reduce Cr(iii) to Cr(ii). But the possibility of such a change appears to be remote for two reasons (i) unlike the chromous hydrazine complex (bluish violet) the chromic complex is bluish green in colour (ii) the chloride in the chromous complex could be fully precipitated by silver nitrate while in the chromic complex only a part of it could be precipitated (see Appendix). As to how the chromic chloride solution in presence of a little hydrazine could act as an indicator electrode for potentiometri work is yet to be seen.

Bromo complexes of Cu(i):

Cuprous bromide formed soluble complexes with HBr, KBr, $MgBr_2$ etc. The composition of the complexes was determined by plotting the solubility data in triangular as well as rectiline coordinate.

The system CuBr-KBr-H_2O was studied at 20°C, the solubility data obtained by the analysis of supernatant liquid were plotted in the triangular coordinates, there was indication of a complex ($KCuBr_2$) in the solid phase and an addition compound CuBr.6KBr in the aqueous phase (page 2 215). A detailed study of the behaviour of cuprous bromide in aqueous KBr at 50°C was also carried out. The chemical analysis of the supernatant liquid showed that the solubilit of CuBr in KBr increased with increasing temprature. Comple ranging from K_4CuBr_5 to $KCuBr_2$ were formed (pp 209-210,2 Tendency of complex ion formation in the aqueous phase was found to be remote and only one complex K_3CuBr_4 might exist The other two ~~complexes~~ complexes CuBr. 5KBr and CuBr. 10KB were probably addition compounds (Fig. 2,3 pp 209-210, 21

The potentiometric and conductometric studies carried out to determine the complex ion formation in the aqueous phase, gave evidence for the formation of compounds like CuBr. 5KBr, CuBr. 10KBr and a complex K_3CuBr_4 (pp 210-21 216).

Analytical studies carried out to determine the comp ion formation between CuBr- HBr (at 50°C) CuBr-$MgBr_2$ (at 2 showed the existence of H_3CuBr_4 and Mg_3CuBr_7 in the solid phase (results were obtained by plotting solubility data i

triangular coordinates (Fig. No. 6, 7 pp 212-213, 218). The inability of Cu^{6+} ions to form definite compounds in aqueous phase might be attributed to the low solubility of CuBr in XBr (X=KH and Mg).

Results on chemical analysis and magnetic susceptibility measurements:

The results on chemical analysis and magnetic susceptibility measurements are included in the Appendix. Most of them substantiate the results of physico-chemical methods although discrepancies were observed in certain cases, e.g., Ethanolamine complexes (Chapter IV) (due to difficulties in isolating them in the pure form). Cu(ii)-chromotrope 2B and Cr(iii)-hydrazine complexes.(p). In the latter two cases presence of orbital magnetism may be responsible for higher values of unpaired electrons as determined from magnetic measurements.

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Analytical and Electrometric studies on the behaviour of cuprous bromide in potassium bromide solution

By Wahid U. Malik, S. M. Fazlur Rahman and Aneesuddin Malik

With 3 Figures

Summary

Chemical studies were carried out to determine the complex ion formation between cuprous bromide and potassium bromide in the aqueous as well as in the solid phase. The formation of complexes in the aqueous phase was also confirmed by potentiometric and conductometric methods. There was no indication of complex formation at room temperature (30 °C). However, at 50 °C rectangular curve showed the formation of complex K_3CuBr_4 and addition compounds like CuBr · 5 KBr; CuBr · 10 KBr in the liquid phase while complexes K_2CuBr_3, K_3CuBr_4, K_4CrBr_5 are formed in the solid phase. The electrometric studies also show the formation of similar complexes in the liquid phase.

Inhaltsübersicht

Es wurde die Bildung von Komplexen aus CuBr und KBr sowohl in wäßriger Lösung als auch als feste Phasen z. T. mit elektrometrischen Methoden untersucht. Bei 30 °C tritt keine Komplexbildung ein; bei 50 °C entstehen die gelösten Verbindungen K_3CuBr_4, CuBr · 5 KBr und CuBr · 10 KBr und als feste Phasen: K_2CuBr_3, K_3CuBr_4 und K_4CuBr_5.

Complex ion formation in the solution of cuprous chloride in hydrochloric acid and potassium chlorid was reported by a number of workers[1–4]) and more recently by HARRIS and co-workers[5]) and MALIK and collaborators[6]). However, no systematic study of the system CuBr–KBr–H_2O had been carried so far, only WELLS and HURLBURT[7]) and

[1]) G. BODLANDER and O. STORBACK, Z. anorg. allg. Chem. **31**, 72 (1902).

[2]) H. REMY and G. LABES, Ber. dtsch. chem. Ges. **66**, 77 (1933).

[3]) L. N. SZABO and Z. SZABO, Z. physik. Chem. **166**, 228 (1933).

[4]) O. A. CHALTKYAN, Zhur. Obschei. Khim, **18**, 1626–1638 (1948).

[5]) C. M. HARRIS, J. Proc. Royal Society, N. S. Wales **82**, 218–224 (1948); **85**, 130 bis 141 (1952).

[6]) W. U. MALIK, S. M. F. RAHMAN and S. A. ALI, Z. anorg. allg. Chem. **299**, 322–327 (1959); **301**, 220–224 (1959).

[7]) H. L. WALES and E. B. HURLBERT, Z. anorg. allg. Chem. **10**, 157 (1895).

FLEURENT[8]) reported the preparation of the compounds $(NH_4)_2CuBr_3$ and K_2CuBr_3 respectively. The present communication describes the formation of complex ions in the solid as well as liquid phase resulted due to the solubility of cuprous bromide in potassium bromide and also due to the equilibrium existing between cuprous bromide and potassium bromide in the aqueous phase.

Experimental

Cuprous bromide was prepared by the method recommended by LEAN and WHATMOUGH[9]). The mixture of copper sulphate and sodium bromide was treated with a stream of sulphur dioxide, small white crystals were formed, they were filtered rapidly and washed with sulphurous acid and alcohol and dried with ether and kept in vacuum desiccator over caustic potash. The resulting crystals were coloured pale greenish yellow. Cuprous ions were estimated by titrating the solutions against ammonium thiocyanate using ferric alum as indicator. Potassium bromide was estimated by precipitating potassium as dipotassium monosodiumcolbalti-nitrite. The amount of KBr was calculated from the weight of the precipitate by multiplying with 238.02/450.1. Comparable results[10]) were obtained by dissolving the cobaltinitrite precipitate in ceric sulphate and estimating the exess of Ce^{++++} ions against ferrous ammonium sulphate potentiometrically. All the experiments

Table 1

B. T. No.	Solution		Original Concentration		Wet residue	
	CuBr gm/lit	KBr gm/lit	CuBr gm/lit	KBr gm/lit	CuBr gm/lit	KBr gm/lit
1	75.2	223.6	75.2	223.6	—	—
2	65.4	185.39	71.4	212.41	6.0	27.02
3	58.2	170.31	67.6	201.22	19.4	30.01
4	41.5	164.3	63.9	190.06	20.4	25.7
5	33.3	152.6	60.2	178.8	26.9	26.2
6	31.6	140.9	56.3	167.7	24.7	26.8
7	26.4	134.6	52.6	156.5	26.2	21.9
8	20.3	128.9	48.8	145.3	28.5	16.4
9	15.87	120.3	45.1	131.1	29.3	10.8
10	8.71	73.03	41.3	122.98	22.6	49.9
11	6.88	70.98	37.5	111.6	30.6	40.7
12	4.9	69.1	33.8	100.6	28.9	30.5
13	3.9	63.4	30.72	88.4	26.8	25.0
14	3.6	62.6	26.3	78.2	22.7	15.6
15	3.2	61.2	21.5	67.08	18.3	5.8
16	2.8	54.8	19.68	55.91	16.8	1.1

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Table 2

Conc. of KBr and CuBr gms/lit in solid phase calc. from tie point	Molar ratio in the solid phase CuBr:KBr	Complexes formed	Molar ratio in aqueous phase calc. from tie line. CuBr:KBr	Complexes formed
40.0 KBr 25.0 CuBr S_1	1:1.8	K_2CuBr_3	1:2.8	K_3CuBr_4
77.0 KBr 33.0 CuBr S_2	1:2.8	K_3CuBr_4	1:5	CuBr · 5 KBr
146.0 KBr 48.0 CuBr S_3	1:3.6	K_4CuBr_5	1:10	CuBr · 10 KBr

were carried out in a thermostat which was maintained at 50 ± 0.1 °C. The bromide solution and water were mixed in the following order:

Boiling tube No. 1 0.0 cc water + 40 cc solution
Boiling tube No. 2 2.0 cc water 38 cc solution
Boiling tube No. 19 36.0 cc water 4.0 cc solution
Boiling tube No. 20 38.0 cc water 2.0 cc solution.

Each boiling tube was covered with a thin layer of paraffin and solution was stirred and allowed to settle. The supernatant liquid was then analysed for CuBr and KBr. The results are as follows see Table 1.

The potentiometric and conductometric studies were done using the same stock solution (as was taken during analytical studies) and all the observations were made with mixtures kept immersed in the thermo static bath at 50 ± 0.1 °C. The cuprous bromide solution and water were mixed in the same order as for the analytical studies.

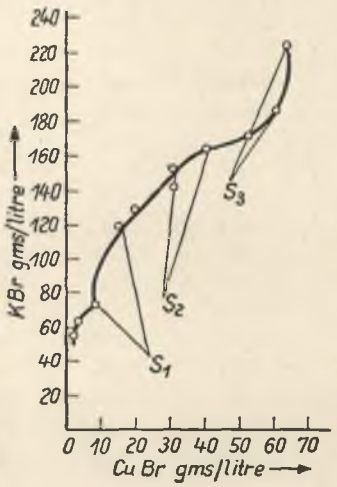

Fig. 1. Phase-diagram

The complexes obtained in the aqueous and solid phases as determined from the phase diagram given in fig. 1

Conductometric studies. The conductance of supernatant liquids were measured

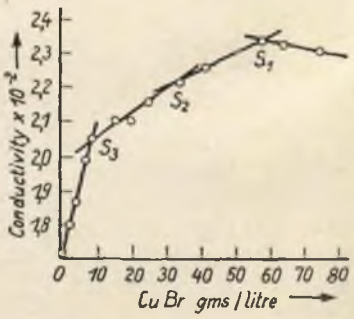

Fig. 2. Conductometric measurements

using a W. T. W. conductivity bridge and dip type conductivity cel for measuring solutions of high conductance a Wheatstone bridge system with a spread of 500 cc wire in

conjunction with W. C. Pye resistance box and oscillator and head phone were used. The electrodes of the cell were platinised before use in order to minimise the polarisation effect. The conductivity curves are shown in fig. 2.

The complex formation found in the aqueous phase by conductivity measurements is as under:

Table 3

Conc. of KBr and CuBr gms/lit at the point intersections		Molar ratio	Complexes formed
73.03 KBr 8.71 CuBr	S_3	1:10	CuBr · 10 KBr
152.15 KBr 33.3 CuBr	S_2	1:5.4	CuBr · 5 KBr
170.31 KBr 58.2 CuBr	S_1	1:2.8	K_3CuBr_4

The conductometric measurements indicate the formation of complex K_3CuBr_4 and addition compounds CuBr · 5 KBr and CuBr · 10 KBr in the aqueous phase thus confirming the results of chemical analysis.

Potentiometric studies

The e. m. f. of the solutions was measured with the help of a clean platinum wire electrode, using the standard calomel electrode as the reference. A Tinsley Vernier potentiometer with a lamp scale galvanometer arrangement was used for determining the potential. In order to check the reversibility of measurements a number of readings were taken for the same sample. The curves are shown in fig. 3.

The results obtained by e. m. f. measurements are as follows see Table 4.

The potentiometric measurements indicate the formation of the complex K_3CuBr_4 and addition compound CuBr · 5 KBr in the aqueous phase.

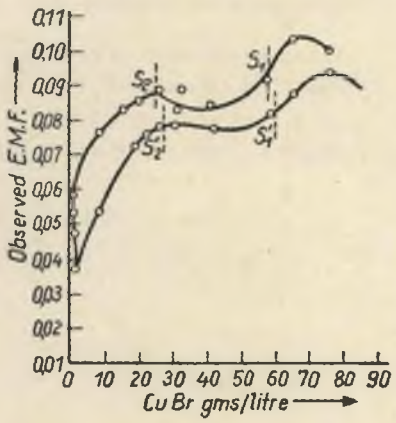

Fig. 3. Potentiometric measurements

Discussion

From the results obtained by the chemical analysis of aqueous phase it may be concluded that at relatively high temperature there is higher solubility of cuprous bromide in potassium bromide, and with increasing concentration of potassium bromide the complexes ranging from K_4CuBr_5 to K_2CuBr_3 are formed, however in solutions there is little tendency of complex ion formation and only the complex K_3CuBr_4 can be said to exist. The other two CuBr · 5 KBr and CuBr · 10 KBr are probably

addition compounds or may indicate the solubility of cuprous bromide in potassium bromide solution. From the chemical analysis and electrometric studies it may thus be concluded that there is the formation of

Table 4

Conc. of CuBr and KBr gms/lit		Molar ratio	Complex formed
58.2 CuBr 170.31 KBr	S_1	1:2.8	K_3CuBr_4
33.3 CuBr 152.6 KBr	S_2	1:5.4	$CuBr \cdot 5\,KBr$
58.2 CuBr 170.31 KBr	S_1'	1:2.8	K_3CuBr_4
41.5 CuBr 164.3 KBr	S_2'	1:4.8	$CuBr \cdot 5\,KBr$

complexes like K_2CuBr_3; K_3CuBr_4 and K_4CuBr_5 in solid phase and the complex K_3CuBr_4 in the aqueous phase.

Further studies are in progress on the phase studies of cuprous chloride, cuprous bromide with alkali and alkaline earth metallic halides.

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